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Introduction to Science Based on Symmetry*

K. R. CHAKRABORTY**

6/12, Central Park, Jadavpur, Calcutta-700 032

In order to comprehend what is "Science Based on Symmetry" it is essential to get acquainted with the mechanism of development of the equilibrium configuration of symmetry as an assembly of five identical regular tetrahedrons and its projected configuration in a plane as a square consisting of 25 identical square units. Deductions from the different inbuilt properties of this configuration can be applied to explain any aspect of the universal phenomenal nature. The talk covers the following important topics :

The concepts of nine digits, the numerical continuum having critical states at 1, 10, 100, 1000, etc. and that of one and zero, have their origin in this configuration.

In the phenomenal nature, the whole square of the total aspects is equal to the sum of the squares of the condensed and uncondensed aspects. They explain progressive evolution of numbers of elements in atomic continuum in periodic system in macrosphere following 2, 2 ; 8, 8 ; 18, 18 ; 32, 32, etc. and the progressive increase of electrons in orbits within the microsphere of atoms following 2, 2 ; 2, 6 ; 2, 6 ; 2, 6, 10 ; 2, 6, 10 ; 2, 6, 10, 14 ; 2, 6, 10, 14, etc.

They give eight forms of transformations (including the one of Lorentz) each having a distinct geometrical configuration. These have been applied in correlating changes in variable properties in thermodynamics and specific heats in terms of changes in temperatures maintaining conservation. In space time transformations they show that both space and time can dilate as well as contract. When Einstein propounded the relativistic relationship, the only form of transformation available to him was that of Lorentz. In the light of the discovery of these forms of transformations there is bound to be rethinking in the entire concept of relativistic science.

They explain dynamic aspect of mechanism of catalytic chemical reactions.

"SYMMETRY" is a very familiar expression generally conveying the sense of uniformity, identicality, perfectly balanced arrangement of things etc. However, one may ponder over questions such as "symmetry of what, amongst what or between what —the implication involving the kind of relativity in similarity or identicality between at least two things. Symmetry among or between ideas ; symmetry among or between things which are static ; or actions which are dynamic may be cited as examples. Progressively deeper and deeper probes in this manner ultimately reveal that the expression in fact is a concept of quantitative significance, having geometrical configuration amenable to quantitative mathematical treatment and deductions from the concept can be applied to explain scientific aspects of phenomenal nature.

The speaker attempts to briefly describe the science based on symmetry in the talk that follows.

Section 1.

Fundamental Configuration of Symmetry

1(a) Suppose a point source of energy radiation radiates rays in a perfectly symmetrical manner in all possible directions from the position of the point source. Conventionally, it is taken for granted that after emission, the rays *at an instant*, will be at equal distances from the point source and the radiated rays will describe a spherical surface with the position of the point source as their centre. As a result, *with respect to the centre*, all the rays residing on the spherical surface will be identical and the emission of rays is symmetrical From the point of view of the *position of the point source*, no doubt, all the rays forming the spherical surface (*at that instant*) would be symmetrical. But, what about the relative status of the individual rays themselves vis-a-vis others while they are on the spherical surface ? Are all other rays identical with respect to any one ray ? Since *with respect to the point source*, which is the cause, its emitted rays, which are the effects, are identical and symmetrical, it is logically expected that each ray would also want the other effect rays to be symmetrical and identical with respect to it. There should not be discrimination in symmetrical relationship between centre vis-a-vis the emanated rays and any individual ray vis-a-vis the other rays on the spherical surface. But at the spherical surface with respect to any ray all the other rays are not symmetrical. Thus all the emanated rays do not, *at an instant*, describe spherical surface front during emission. We, therefore, require to find an alternative configuration for the rays (at an instant) which will symmetrically satisfy both the point source as well as the emanated rays among themselves. There is only one configuration, namely, a regular tetrahedral mode, which would completely satisfy both the source at the centre and the 4 rays (at an

* Acharya J. C. Ghosh Memorial Lecture (1978) delivered under the auspices of the Indian Chemical Society on September 4, 1981 at Calcutta.
** Ex-Managing Director, Fertiliser Corporation of India, New Delhi.

instant) occupying the 4 corner positions of the tetrahedron. Thus *with respect to any ray* the other 3 rays will be symmetrical and identical and with respect to the centre the 4 emanated rays are identical. In other words the point source has 4 directional symmetry and each ray has three directional symmetry. This is the picture, *at an instant*, during emission. To oppose this action of the point-source and to get an equilibrium configuration, each of the four identical equilateral triangular faces must be opposed (as reaction) face to face by one identical regular tetrahedron. The action of the central one is due to energy and the reaction of the outer ones is due to matter significance. Thus the equilibrium configuration consists of a unit package of 5 regular tetrahedrons : one at the centre and 4 outer ones placed against the four equilateral triangular faces of the one at the centre. One can call this as an unit universal wave or unit square wave or can call this as a quantum of unit configuration of the Universe in its miniature form, just like a seed and a tree. We shall call this as fundamental configuration of symmetry or simply configuration of symmetry. The central tetrahedron represents (action) energy radiation and the four opposing outer tetrahedrons represent matter significance as reactions to the action of the former. A tetrahedron when projected on a plane passing through the centre and parallel to a pair of opposite sides is a square (Fig. 1) in the plane.

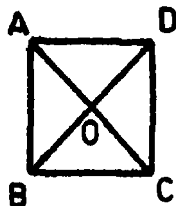


Fig. 1

Similarly, the composite configuration of 5 tetrahedrons, when projected on a plane passing through the centre and parallel to a pair of two opposite sides of the central tetrahedron would also be projected as a square as shown in Fig. 2.

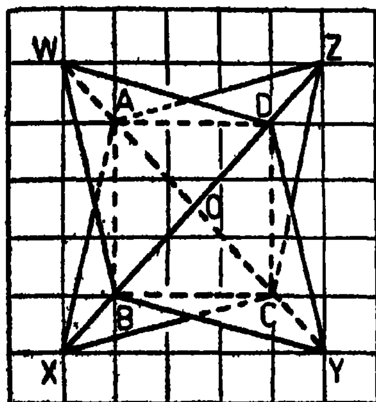


Fig. 2

The Fig. 2 thus, when expressed in terms of identical square units on the plane generates a square comprising 25 identical square units as shown in Fig. 3. This is derived from the inbuilt magnitudes of the dimensions in a regular tetrahedron. For example, in a regular tetrahedron if the magnitude of distance between the centre and centre of the triangular faces is 1, the distance between the

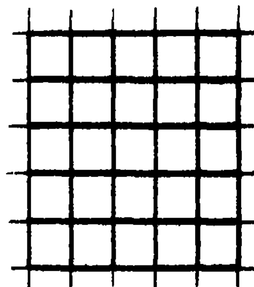


Fig. 3

centre and the corner positions is 3, the distance between a corner position and centre of the opposite triangular face is $3+1=4$. When a regular tetrahedron is placed against one equilateral triangular face of the central tetrahedron, the distance between the centre of the central tetrahedron and apex corner position of the outer tetrahedron is $1+4=5$. Applying these data, we get the projected square comprising 25 identical square units, the two diagonals will have $(10+10)=20$ identical units of distance of diagonals and 4 sides of the square will have 20 identical units of distance $(5+5+5+5)$ of sides (Fig. 4). This square configuration consisting of 25 identical square units has 9 diagonals and 10

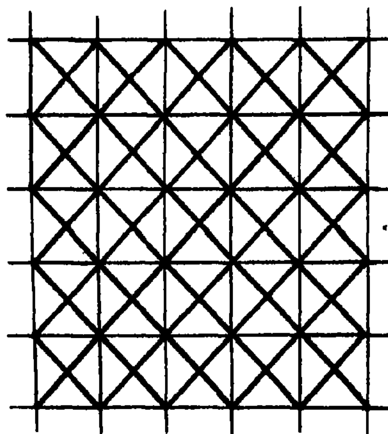


Fig. 4

equal linear units on the central diagonal (Figs. 6 and 7). Fig. 5 shows the arrangement of the square units in the configuration of 25 ; there are 8 units in four pairs in continuity of the central square unit and there are 4 times 4 units along the 4 divergent directions of the two diagonals which are discontinuous with respect to the central unit.

Further, it may be noticed that when the configuration expands, the size of the new square units

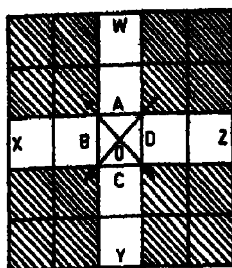


Fig. 5

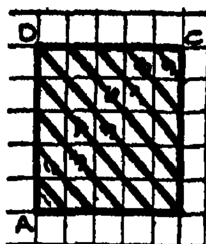


Fig. 6

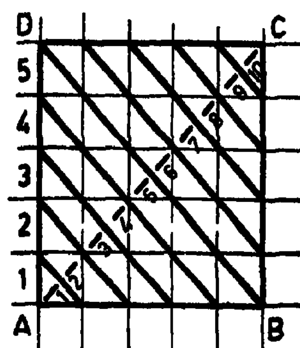


Fig. 7

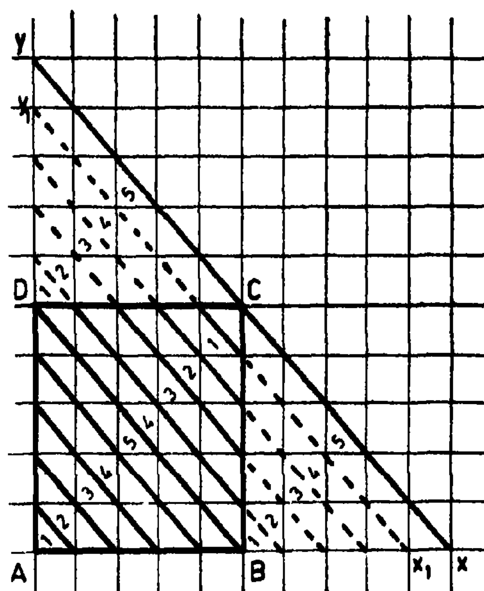


Fig. 8

to be added in continuity of the central unit always maintain constant magnitude of size of each unit. But in the diverging 4 directions towards the corners along the diagonals, the size of square units can vary. This aspect of continuity and discontinuity, it may be noted, will play important role in the development of science based on symmetry.

1(b) *Some of the important properties of the fundamental configuration of symmetry :*

Digits and numerical continuum : From a glance at the fundamental configuration of symmetry (Figs. 6 and 7) comprising 25 identical square units it can be seen that in between two opposite corner positions there are nine finite diagonals, situated apart at equal units of linear distances numbering 10 on the main diagonal. But the number of identical units on each side is always 5.

Numerically, the sum of the roots of two squares of 5 units of side is equal to root of square of 10 units of diagonal :

$$\sqrt{5^2} + \sqrt{5^2} = \sqrt{10^2}.$$

It should be noted that the magnitude of units on the left hand side is different from the units on right hand side. Actually $\sqrt{2}$ unit of side is equal to one unit of diagonal.

In the square ABCD, the magnitudes of the 9 diagonals vary in an undulatory mode in the square configuration. Thus the magnitudes of diagonals (Fig. 8) within the square configuration ABCD increase progressively starting with zero at A and then as 1, 2, 3, 4 reaches maximum of 5 at BD after which they progressively decrease as 4, 3, 2, 1 and zero at C. But on either of the outer sides of the configuration the magnitudes increase as shown by dotted lines as two times 1, 2, 3, 4 and 5. Thus the magnitude of the diagonal passing through C is 5+5=10. In this manner the numerical continuum develops in magnitude. The numerical continuum on this basis is shown in Fig. 9.

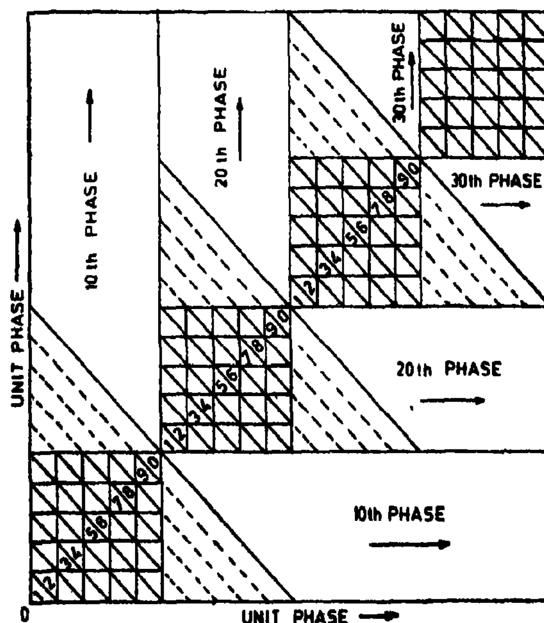


Fig. 9. Evolution of numbers from square continuum in one direction.

It should be emphasised that *the method of derivation of the fundamental configuration of symmetry as a package unit of 5 regular tetrahedrons and their projected square configuration in a plane consisting of 25 identical square units were the basis for the development* of 9 and only 9 digits, 10 magnitudes, concepts of zero and one, and the

numerical continuum as unit, 10, 100, 1000 etc. etc., have been possible. A significant aspect should be realised that the numerical continuum is not a uniform continuity as far as digits are concerned. The digits start with least magnitude in a phase and rise to maximum in that phase. Again the digits, in a higher phase, starts with least and rises to maximum. This process is repeated as the numerical magnitudes increase in terms of higher and higher magnitudes of phase continuum as unit, 10, 100, 1000, 10000, etc. etc or as unit, 10, 20, 30, 40, . These states are designated as critical states.

1(c). *Criteria for development of square continuum of identical square units in a plane are the operation of the 4 symbols +, −, ×, ÷ :*

1+1=2	2+2=4	3+3=6	4+4=8
1−1=0	2−2=0	3−3=0	4−4=0
1×1=1	2×2=4	3×3=9	4×4=16
1÷1=1	2÷2=1	3÷3=1	4÷4=1 and so on.
Sum total is $4=2^2$	Sum total is $9=3^2$	Sum total is $16=4^2$	Sum total is $25=5^2$

Let us start with zero and following the identical procedure as above, we get the series :

$$0+0=0$$
$$0-0=0$$
$$0\times 0=0$$
$$0\div 0=1$$

whose sum total is 1^2

As per the above criteria the development of increasing square magnitudes in a plane are :

$$1^2, 2^2, 3^2, 4^2, 5^2, \ldots\ldots$$

Therefore $0 \div 0 = 1$ and is not *indeterminate.* It can be called oneness.

From this one can realise that zero is an abstract concept, which has no configuration, whose magnitude is nil or nothing, which cannot cause anything, which has no root but whose homogeneity or identicality or oneness contributes to the concept of one. When zero assumes the power of anything that is reduced to one. One is also an abstract concept, which has *no cause* ; *it itself is its own* cause and it is the cause of all others. It has no root, it itself is its root. It has configuration but that can assume any magnitude. It is powerless and anything which is powerless is reduced to one. Unless one assume the power of everything, objective existence is not possible. Unless one whole is differentiated into finite parts, the objective concept of existence cannot be realised or described.

1(d). *Swastika method of development of square towards increase in magnitude or decrease in magnitude :*

There are many methods of development of square configuration from lower to higher magnitudes or from higher to lower. Swastika method in Fig. 10 is the most generalised method among others.

The generalised formula is :

$$4\left[\frac{\phi b-\phi a}{2}+\phi a\right]\left[\frac{\phi b-\phi a}{2}\right]+\phi a^2=(\phi b)^2 \quad \text{. Eq. 1.}$$

$$\text{or,}\quad \left[\frac{4(\phi b+\phi a)}{2}\right]\left[\frac{\phi b-\phi a}{2}\right]+(\phi a)^2=(\phi b)^2$$

'a' and 'b' can be magnitude of any function. It can be linear, square, root, numbers, cumulatives etc. Let ϕb be greater than ϕa. In the above formula when $(\phi a)^2=0$, Fig. 10(a) becomes the Fig. 10(b).

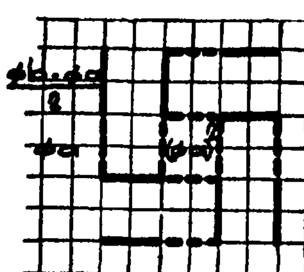


Fig. 10a

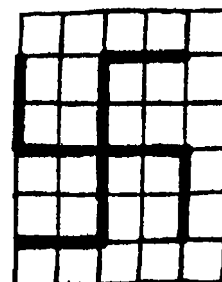


Fig. 10b

Illustrations : Suppose we want to increase 2^2 to 6^2, we will have $4\left[\frac{(6-2)}{2}+2\right]\left[\frac{6-2}{2}\right]+2^2$

$$\text{or } 4.(4).(2)+2^2=32+2^2=6^2$$

In the reverse case, suppose we want to decrease 7^2 to 2^2 we will have

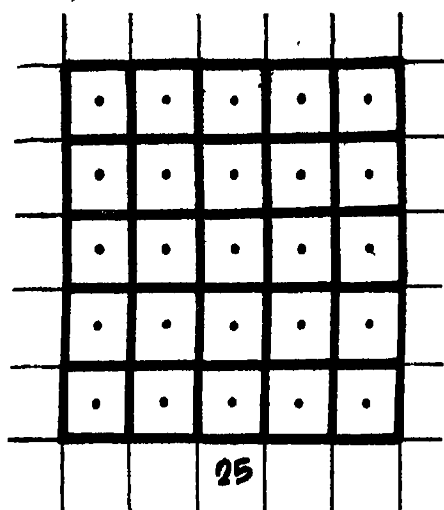
$$4\left[\frac{(2+7)}{2}\right]\left[\frac{2-7}{2}\right]+7^2$$

$$\text{or } (9).(-5)+49=49-45=4=2^2$$

Two ways of expressing a square configuration : $a\times a=a^2$ where a is side of the square ; and $2\Sigma(a-1)+a=a^2$ where a = number of identical square units along the central diagonal.

1(e) *Differentiation of whole square into condensed square and uncondensed square :*

Suppose each of the 25 square units of the configuration is condensed to points of position at the centre of each square unit. There will then be 25 condensed points of positions and by linking these they generate 16 indentical condensed square units (Fig. 11). The total whole square of 25 units minus 16 condensed square units leaves out 9 square units uncondensed. Thus total whole square is 25, condensed whole square is 16 and uncondensed whole square is 9. Thus $5^2-4^2=3^2$. If the central uncondensable square unit could be condensed to one point of position, that could only generate a point of nil square magnitude. The relationship in that case would be $1^2-0^2=1^2$. In this way the whole configuration will progressively develop in 4 directions as in the following [Figs. 13(a) and 14] :



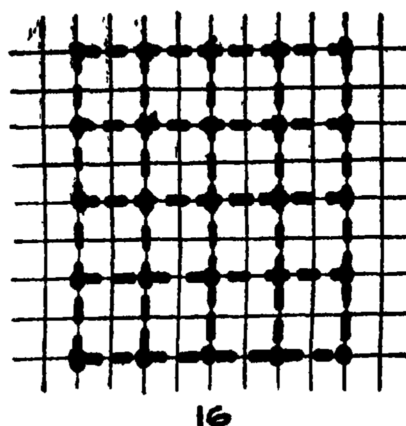


Fig. 11

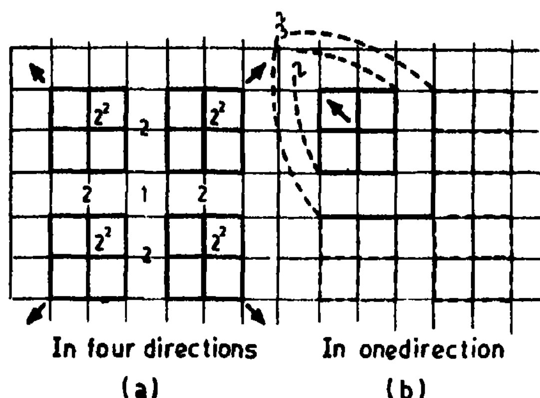


Fig. 13

Table 1

Total whole square		Condensed square		Uncondensed square
1^2	-	0^2	=	1^2
5^2	-	4^2	=	3^2
13^2	-	12^2	=	5^2
25^2	-	24^2	=	7^2
...		...		...

The above series can be expressed by the following relationships .

(i) $(4\Sigma N+1)^2-(4\Sigma N)^2=(2N+1)^2$ ... Eq. 2.
where N can assume magnitudes 0, 1, 2, 3, 4, ...

(ii) $(a^2+b^2)^2-4a^2b^2=(a^2-b^2)^2$ .. Eq. 3.
where a is greater than b by unity.

Since the above deductions are in four directions and square development in each direction is identical, the development in any one direction is as in Table 2.

It shall be noted from Fig. 13(b), 15 and 16 that uncondensed square units in one direction are the roots of total whole square in 4 directions. In this manner many significant deductions can be mentioned. We shall mention here only a few important cases.

Table 2

Total whole square		Condensed square		Uncondensed square
1^2	-	0^2	=	$(\sqrt{1})^2$
3^2	-	2^2	=	$(\sqrt{5})^2$
7^2	-	6^2	=	$(\sqrt{13})^2$
13^2	-	12^2	=	$(\sqrt{25})^2$
21^2	-	20^2	=	$(\sqrt{41})^2$
...		...		...

Formula $(2\Sigma N+1)^2-(2\Sigma N)^2=\sqrt{(4\Sigma N+1)}^2$ .. Eq. 4

(a) In the configuration of symmetry and the continuum of square waves, sum of the number of square units at the starting front, in four directions, and finishing front is a square.

Table 3

Total whole square	Square units in front	
1^2	0	
		4^2
5^2	16	
		8^2
13^2	48	
		12^2
25^2	96	
		16^2
41^2	160	

(b) The sum of the roots of total whole square and condensed whole square is equal to uncondensed whole square in four directions.

Table 4

Root of total whole square		Root of condensed whole square		Uncondensed whole square
$\sqrt{1^2}$	+	$\sqrt{0^2}$	=	1^2
$\sqrt{5^2}$	+	$\sqrt{4^2}$	=	3^2
$\sqrt{13^2}$	+	$\sqrt{12^2}$	=	5^2
$\sqrt{25^2}$	+	$\sqrt{24^2}$	=	7^2
$\sqrt{41^2}$	+	$\sqrt{40^2}$	=	9^2
...		...		...

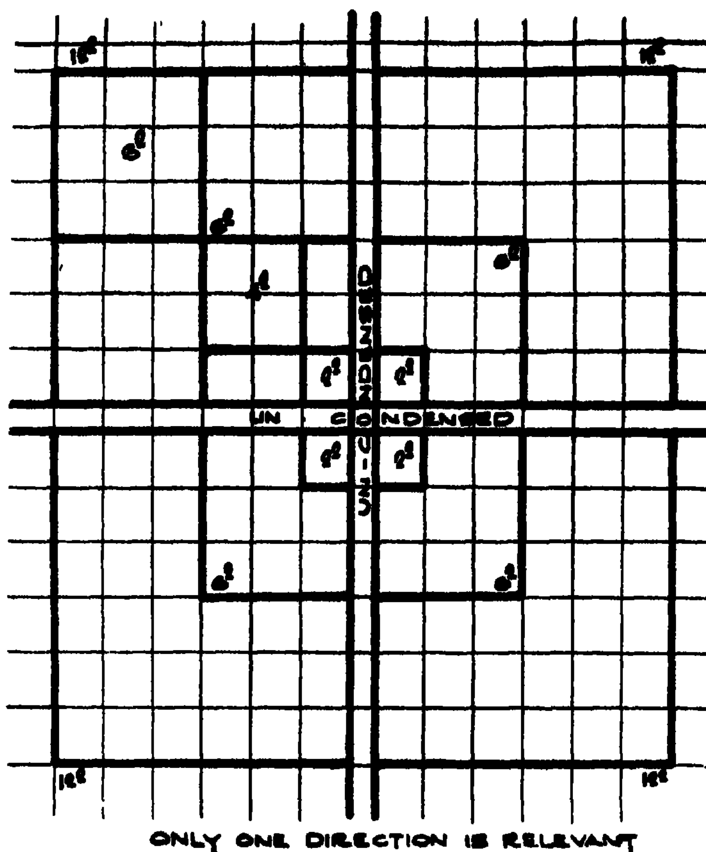

UN-CONDENSED
UN CONDENSED
ONLY ONE DIRECTION IS RELEVANT

Fig. 14

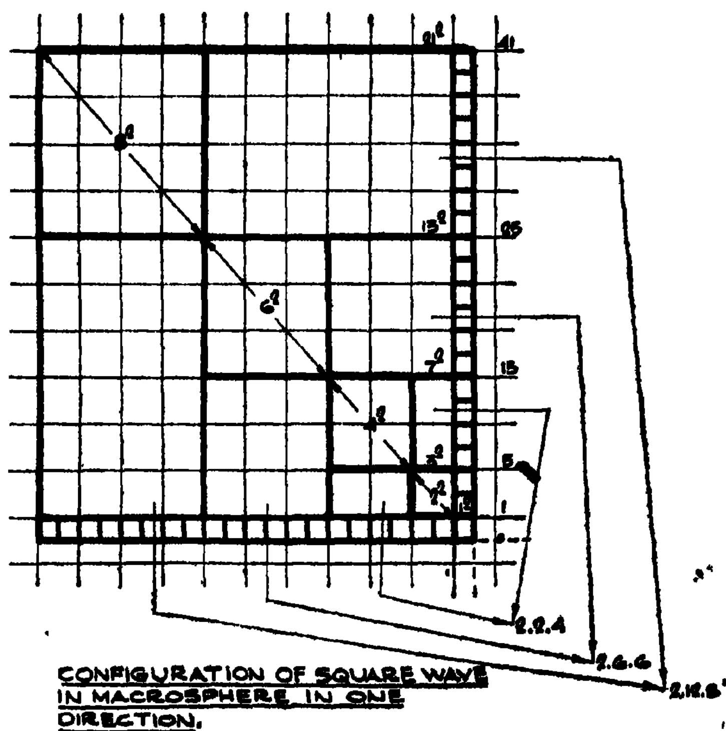
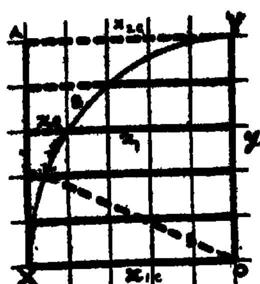
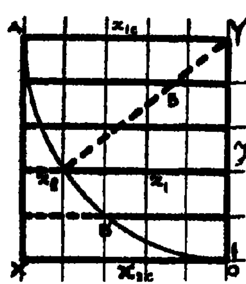
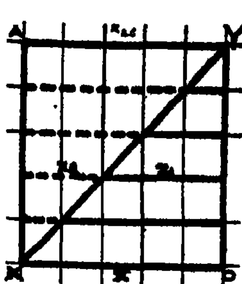
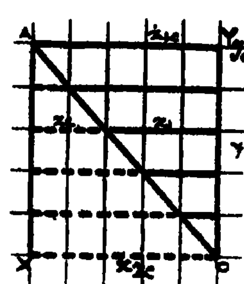

CONFIGURATION OF SQUARE WAVE IN MACROSPHERE IN ONE DIRECTION.

Fig. 15


Fig. 12(a)


Fig. 12(b)


Fig. 12(c)


Fig. 12(d)

The above deductions giving three whole square relationships are unique in the sense that universal square waves propagate in *terms of whole (not in parts or fractions) squares* from a lower state to a higher state. The concept is similar to the *concept of quanta.*

(c) Figs. 15 and 16 show that in one direction, excluding the uncondensed square units in continuation of central square, total square groups in combination of both condensed and uncondensed in sequence increase as 1.2^2, 2.4^2, 3.6^2, 4.8^2, ...

1(f) *Variation in forms of transformation of changes in properties of two dimensions, in equilibrium combination, between critical states within constant whole square, maintaining conservation :*

One of the most important consequences derived from the *configuration of symmetry* is the progressive development of higher magnitudes of square waves in the universal context. The relationships have been presented in Table 1. Let us confine to the square configuration of 25 square units of configuration of symmetry and refer to Figs. 12(a), 12(b), (12(c) and 12(d).

Total whole square	−	Condensed whole square	=	Uncondensed whole square
1^2	−	0^2	=	1^2
5^2	−	4^2	=	3^2

The total whole square remaining constant as 5^2, changes in the magnitudes of condensed x_1 and uncondensed x_2 vary in combination together along one axis say, horizontal axis OX maintaining conservation i.e., $x_1+x_2=5$. They vary, with respect to variation of a dimension y along the vertical axis OY, from zero at to O maximum 5 at Y where the dimension y will attain critical, constant maximum value y_c. This is shown in Figs. 12(a), (b), (c) and (d). In these figures the two magnitudes of changes of x_1 and x_2 vary together between the bottom and top sides maintaining conservation, in such a way that if at the bottom side OX, one of them x_1 will be zero and the other x_2 will be equal to the side OX, i.e., the maximum critical value as x_{2c}. At the top side, similarly if $x_2=0$ $x_1=x_{1c}$ maximum constant critical value. The bottom side of the square is one critical state and the top side of the square is another critical state. Above the top critical state there can be one or more critical states but the nature of those phases in combination will be different from x_1 and x_2 combination. Similarly below the bottom critical state there can be one or more critical states wherein also the phases, in combination will vary together but they will be different from x_1x_2 combination. In between the two critical states changes of properties of the two components x_1 and x_2 will vary in two zones separated either by a circular line with radius 5 as in Figs. 12(a) and 12(b) or they may be separated by the diagonal of the square as shown in Figs. 12(c) and 12(d). The form of relationships of x_1 and x_2 in the four configurations would be as in Table 5.

TABLE 5

i(a).	$x_1/x_{1c}=\sqrt{(y_c^2-y^2)/y_c^2}$	i(b).	$x_2/x_{2c}=1-\sqrt{(y_c^2-y^2)/y_c^2}$	Fig. 12(a).
ii(a).	$x_1/x_{1c}=\sqrt{\{y_c^2-(y_c-y)^2\}/y_c^2}$	ii(b).	$x_2/x_{2c}=1-\sqrt{\{y_c^2-(y_c-y)^2\}/y_c^2}$	Fig. 12(b).
iii(a).	$x_1/x_{1c}=(y_c-y)/y_c$	iii(b).	$x_2/x_{2c}=1-(y_c-y)/y_c$	Fig. 12(c)
iv(a).	$x_1/x_{1c}=\{y_c-(y_c-y)\}/y_c$	iv(b).	$x_2/x_{2c}=1-\{y_c-(y_c-y)\}/y_c$	Fig. 12(d)

It should be noted here that the form of relationship in equation i(a) has the same form of the famous Lorentz transformation for length contraction, and equation i(b) is the form of transformation for time dilation. All these forms have been verified by employing established data in the subsequent sections.

Section 2

Application in Phenomenal Nature : Macrosphere and Microsphere

The universal nature is phenomenal; some aspects in it are distinguishable while some others

are indistinguishable or unobservable. The phenomenal nature cannot be wholly distinguishable or wholly unobservable. The universal nature exists always as an equilibrium combination of both these aspects. Nature is an ever changing entity. The change takes place in terms of progressively changing phase combinations through critical states towards either (Fig. 5) directions (higher or lower). In the fundamental configuration of symmetry the square units in continuation of the central square unit are most indistinguishable or uncondensable and 4 times 4 square units along diagonal are most segregated or condensed units (say atomic configurations). It may be noted that Fig. 11 gives 3^2 as uncondensed. Fig. 5 also gives 9 square units in continuation of and including the central one uncondensed.

The significance of critical state in the present context is identical with vapour liquid critical state of H_2O at 705.4°F through which vapour and liquid phase combination of H_2O changes to H_2O as permanent gas above 705.4°F. In the reverse direction, when H_2O as permanent gas is cooled below the critical temperature two phases namely, liquid H_2O and vapour H_2O in equilibrium combination, are formed. The above relates to macrosphere of Universal Nature only. As we have stated, the universal nature contains two opposite kinds of phenomenal development, one is macrosphere and the other is microsphere. The planets, galaxies, nebula, quasar, atomic continuum, plant and animal domains etc etc. are macrospheric phenomenal manifestations. The microspheric development takes place within a constant configuration. The development of electrons in orbits indefinitely within atomic configurations, which remain constant, is a microspheric phenomenon. Thus as far as the chemical elements are concerned in macrosphere, number of elements progressively develops in free space ; while in the other case, the atomic configuration remaining constant, the number of electrons progressively develops in the atomic orbits within the microsphere of atoms.

2(a) *Macrospheric development and periodic classification of elements :*

Since, square wave developments, in each of the 4 directions, are identical, we shall deal with the continuum in one direction to investigate the phenomenal nature of square wave development in one direction. This has been deduced in Figs. 15 and 16 employing condensed, uncondensed and total whole relationship in Table 2.

For easy understanding, the nature of square waves in sequence as detailed group-wise in Fig. 16 have been shown in Table 6 in which they are arranged horizontally, so that each horizontal column containing square and rectangular groups in one square wave and these can be termed as B wave, C wave, D wave, E wave etc. There is no wave of A because it is wholly uncondensed. In the other waves the groups containing A_1, A_2, A_3 etc. at the both ends of the horizontal columns of the square waves are uncondensed. In other words, the two ends of each wave are zero or nil waves. Leaving out the square units in A's continuity, the square magnitudes in increasing order of magnitude of waves in sequence are 1.2^2, 2.4^2, 3.6^2, 4.8^2,

TABLE 6

8.1^2 A_4	8.2 B_3	8.4 C_2	8.6 D_1	8^2 E	8.6 D_1	8.4 C_2	8.2 B_3	8.1^2 A_4
	6.1^2 A_3	6.2 B_2	6.4 C_1	6^2 D	6.4 C_1	6.2 B_2	6.1^2 A_3	
		4.1^2 A_2	4.2 B_1	4^2 C	4.2 B_1	4.1^2 A_2		
			2.1^2 A_1	2^2 B	2.1^2 A_1			
				1^2 A				

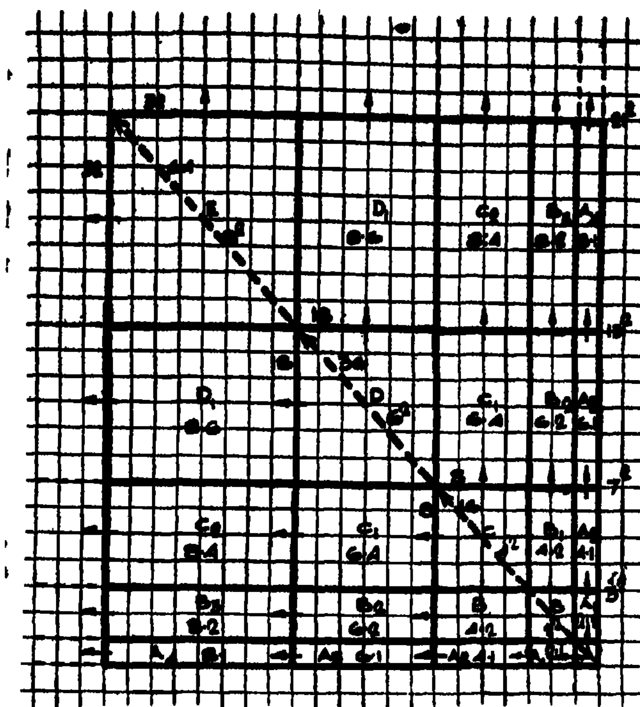


Fig. 16

Along the diagonal progressively more and more denser and segregated condensed matter elements develop as 2^2, 4^2, 6^2, 8^2, . . in the universal context. In continuity of A, energy intensity progressively decreases as the numbers of square units increase. In between these two extreme states the intermediate phase groups exist, containing both matter and energy in combination. To maintain symmetry the squares along the diagonal will require to be split in two halves, one half for the left wing and the other for the right wing of a particular wave. This is shown in Fig. 18. Thus the number of chemical elements progressively develop as 2,2 ; 8,8 ; 18,18 ; 32,32 and so on. These aspects are elaborated in Fig. 18 and the periodic classification of elements in this approach has been shown in Fig. 19(a) and Fig. 19(b). (For detailed analysis refer to "Science Based on Symmetry"*, Chapter 3).

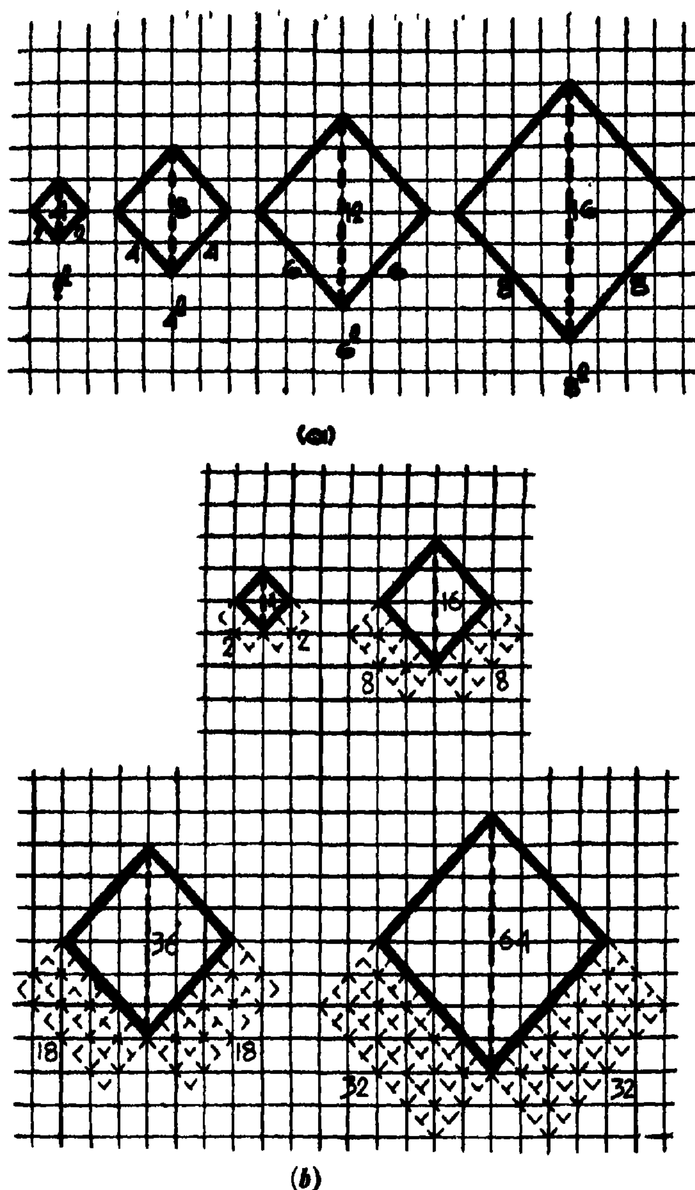
We do not intend to go into a detailed discussion on how the waves progressively develop more and more condensed phases while passing through critical states. We are mentioning some essential points, which are different from conventional classification. In this classification we cannot use the conventional atomic numbers, because here the first group (Fig. 19) contains 4 elements as against 2 in the conventional classification. The number 4 as 2^2 for the first group arises from the consideration of the square wave continuum developed from configuration of symmetry, in which two numbers only in the first group cannot be reconciled.

Therefore our assigned numbers for the elements will be two more than the conventional atomic numbers.

In the absence of any other data, to fill up the 4 positions we have suggested *ortho-* and *para*-hydrogen as two elements and neutron as an inert gas. Many properties of *ortho-* and *para*-hydrogen and of neutron suggest this approach. But it may be argued that *ortho*-hydrogen and *para*-hydrogen refer only to two molecular states of a single atomic species of hydrogen and that a neutron has got no detectable orbital electron. Nevertheless, it is asserted that if the theory propounded here, on the basis of configuration of symmetry, is correct the number of lighter elements ending with Helium, must comprise four members and not two. It is possible that with improved experimental techniques, discoveries may be made of a sub-hydrogenic element or perhaps distinguishing features in the atomic state which lead to the formation of molecular *ortho-* and *para*-hydrogen, and also of further details of the structure, which will confirm the validity of this hypothesis. In the absence of any other data we continue to use *ortho-* and *para*-hydrogen as two elements and neutron as an inert gas.

There could be another explanation. *Ortho* and *para* could represent combination of two opposite phases (periods) in the first group, just as every subsequent group consists of two periods. In similarity with H_2O as liquid and vapour combination, *ortho* and *para* may be two similar phase combination. At higher temperature vapour

* K. R. Chakravorty, "Science Based on Symmetry", FIRMA KLM(P) Ltd., Calcutta-12, 1977.



(a)

(b)

Fig. 18

density increases and liquid density decreases. At vap.-liq. critical state liquid phase is eliminated. Similarly, at lower temperature liquid density increases and vapour density decreases and at a certain lower critical temperature near about 4°C the liquid density is the highest and vapour density is negligible. In like manner, *ortho* % in equilibrium mixture increases with increase in temperature and *para* % decreases; and *ortho* % decreases and *para* % increases with decrease of temperature. At 20°K almost the whole is *para* (99.82%). Just as liquid and vapour phases have opposite properties, *ortho* and *para* also have certain opposite characteristics. Thus, *para* has antisymmetric nuclear spin function, whereas *ortho* has symmetric nuclear spin function. *Para* has only even rotational states while *ortho* has only odd rotational states. These are some suggestions which may be considered in order to see whether *ortho* and *para* can fit in the first group of four elements. The number of chemical elements in the first group as four has been settled by the configuration of symmetry itself as 2^2.

While discussing the periodic classification of elements, Fyenman stated that it was necessary to find solutions of the form $\psi=f(r_1, r_2)e^{-(i/h)ET}$ to obtain the stationery states and energy levels as the geometrical dependence is contained in f, which is a function of six variables—the simultaneous positions of the two electrons but no one has found an analytical solution though solution for the lowest energy states has been obtained by numerical methods. According to him, it is hopeless to try to obtain exact solutions with 3, 4 or 5 electrons and it would be going too far to say that quantum mechanics has given a precise understanding of the periodic table.

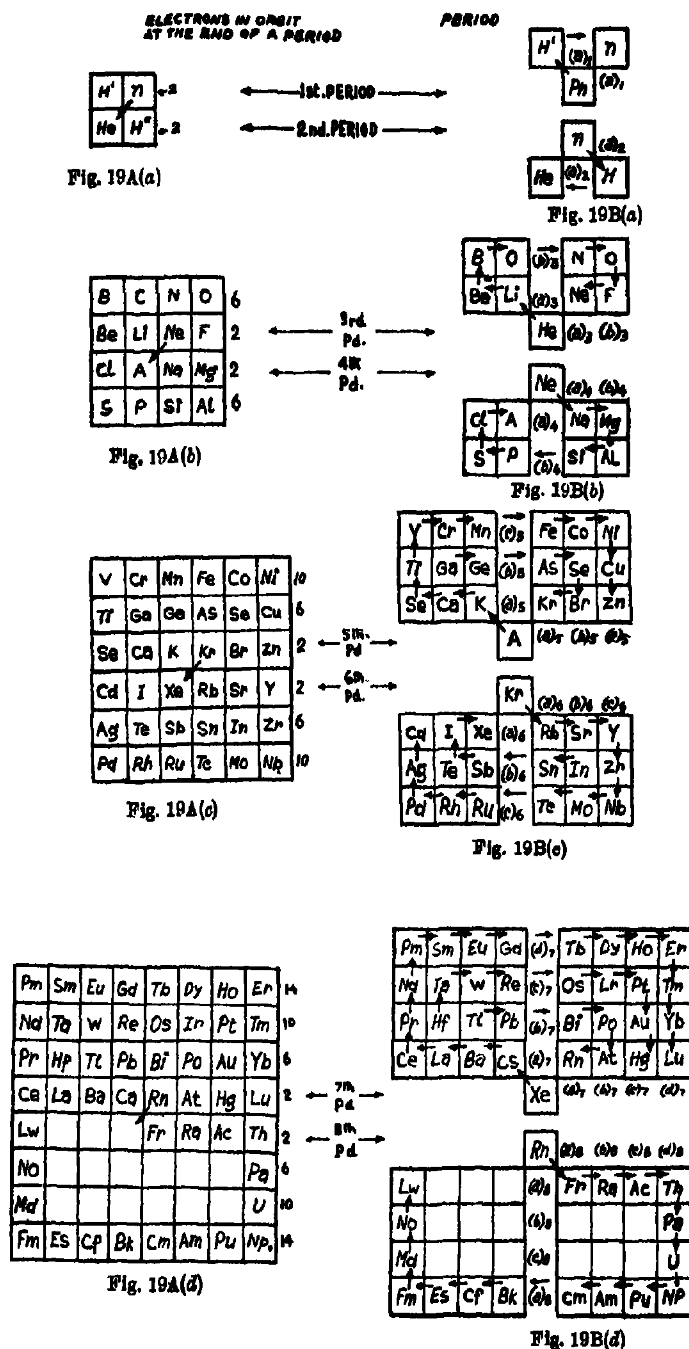


Fig. 19. Periodic table of elements as per evolution in plane square continuum.

We are not including detailed discussion on wave mechanism based on symmetry, as per our approach, because the scope is limited for the present purpose. Therefore in the following we are mentioning only a few relevant conclusions on the nature of matter energy wave, connected with the periodic classification of elements. (For details refer to "Science Based on Symmetry", Chapter 6).

(i) The magnitudes of condensed waves in nature progressively develop in terms of increasing integral multiples of square of increasing magnitudes of maximum amplitudes as even numbers. (Refer to Fig. 16 and Table 6). For example :

B wave	C wave	D wave	E wave	
1.2^2	2.4^2	3.6^2	4.8^2	and so on.

(ii) The nature of development of the wave lengths can be expressed as the magnitudes of the average wave lengths of waves in nature progressively develop in terms of increasing integral multiples of maximum amplitudes, which must be even magnitudes. For example take D wave.

Starting state $\left|\begin{matrix}B_2\\2,\end{matrix}\right|\begin{matrix}C_1\\4,\end{matrix}\left|\begin{matrix}D\\0,\end{matrix}\right|\begin{matrix}C_1\\4,\end{matrix}\left|\begin{matrix}B_2\\2\end{matrix}\right|$ finishing state $\left|\begin{matrix}B_2\\2\end{matrix}\right|\begin{matrix}C_1\\4\end{matrix}\left|\begin{matrix}D\\6,\ 6\end{matrix}\right|\begin{matrix}C_1\\4\end{matrix}\left|\begin{matrix}B_2\\2\end{matrix}\right|$

average $\left|\begin{matrix}B_2\\2\end{matrix}\right|\begin{matrix}C_1\\4\end{matrix}\left|\begin{matrix}D\\3,\ 3\end{matrix}\right|\begin{matrix}C_1\\4\end{matrix}\left|\begin{matrix}B_2\\2\end{matrix}\right|$

$=18.$

(iii) The maximum amplitudes decide the whole wave as well as its wave length and ratio of whole wave magnitude and the magnitude of average wave length gives magnitude of maximum amplitude of the waves. For example :

$\frac{1.2^2}{1.2}, \frac{2.4^2}{2.4}, \frac{3.6^2}{3.6}, \frac{4.8^2}{4.8}, \ldots$ = maximum amplitudes 2, 4, 6, 8, ...

(iv) Magnitude of each half of the square of maximum amplitude is identified with magnitude of average wave length. For example :

$2^2, 4^2, 6^2, 8^2, \ldots = 2+2,\ 8+8,\ 18+18,\ 32+32,$

Average wave lengths $= 2, 8, 18, 32, \ldots$

(v) Every group in the periodic table of elements represents square of maximum amplitude of a condensed wave of nature in wave continuum in the universal context. The squares of maximum amplitudes represent the magnitudes of total numbers of elements in the groups, each comprising two periods. The magnitude of numbers of elements in each period of a group represent magnitude of average wave length of the corresponding condensed wave of nature. Square of max. amplitude : $2^2, 4^2, 6^2, 8^2, \ldots$ = number of elements in groups. Number of elements in two periods in each group are 2, 2 ; 8, 8 ; 18, 18 ; 32, 32 ; ..

(vi) The increase in the total number of elements from a previous to the next group in sequence in the periodic table occurs in terms of two times the sum of maximum amplitudes of the previous and the next waves. For example :

$2(0+2)$ A→B wave ; or as 2, 2 ; $2(2+4)$ B wave→C wave ; 6, 6 ; $2(4+6)$ C wave→D wave ; 10, 10 ; $2(6+8)$ ... . D wave→E wave ; 14, 14 ; ....

2(b) *Microspheric development and electronic structure of atomic configuration :*

Like the macrospheric development, there are three square relationships in the case of microspheric development also. It starts with 9 square units from the 25 square units of configuration of symmetry in one direction, in which there are 5 uncondensed and 4 condensed making the total whole as 3^2. [Figs. 17(b), 20 and 21].

Progressively developing series in the microspheric case will be as in Table 6(a).

TABLE 6(a)

Total whole square		Condensed		Uncondensed
3^2	=	4.1^2	+	5.1^2
6^2	=	4.2^2	+	5.2^2
9^2	=	4.3^2	+	5.3^2
12^2	=	4.4^2	+	5.4^2
...		...		...

The roots of three square relationship in microsphere will be root of total whole square minus root of condensed whole square and is equal to root of uncondensed minus condensed square as shown in Table 6(b).

TABLE 6(b)

Root of Total whole square		Root of Condensed whole square		Root of Uncondensed – Condensed square
$\sqrt{9}$	−	$\sqrt{4}$	=	$\sqrt{1^2}$
$\sqrt{36}$	−	$\sqrt{16}$	=	$\sqrt{2^2}$
$\sqrt{81}$	−	$\sqrt{36}$	=	$\sqrt{3^2}$
$\sqrt{144}$	−	$\sqrt{64}$	=	$\sqrt{4^2}$
...		...		...

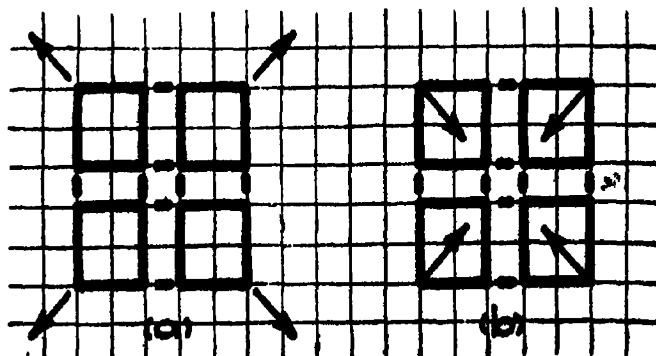


Fig. 17

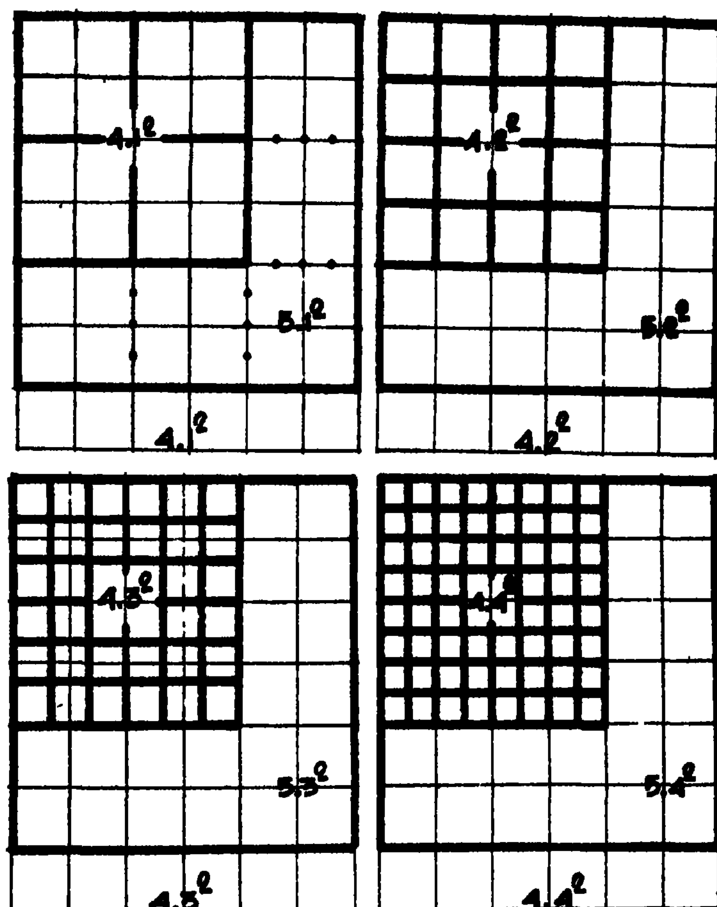

4.1²
5.1²
4.1²
4.2²
5.2²
4.2²
4.3²
5.3²
4.3²
4.4²
5.4²
4.4²
MICRO SPHERE OF CONDENSED

Fig. 20

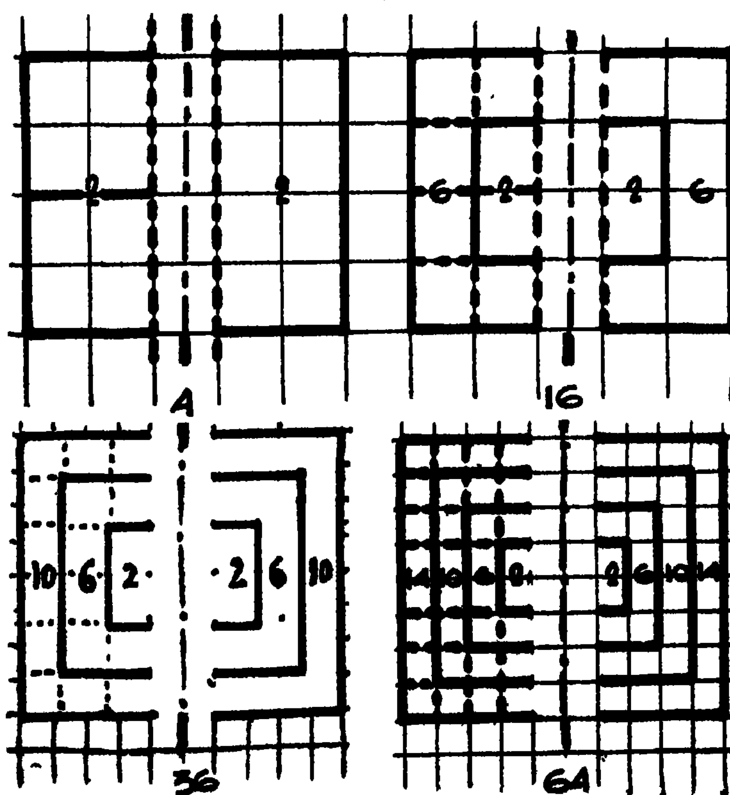

2
2
4
6
2
2
6
16
10
6
2
2
6
10
36
14
10
6
2
2
6
10
14
64

Fig. 21

There could be a valid question that while the macrosphere can develop indefinitely, there must be some scope available for microspheric development also—within a constant atomic configuration. That this is so is illustrated by following relationship :

$$\frac{\text{Total whole square}}{\text{Uncondensed} - \text{Condensed square}} = \frac{3^2}{1^2}, \frac{6^2}{2^2}, \frac{9^2}{3^2}, \frac{12^2}{4^2} = 9$$

Period	Element number	Element	a_1	a_2	b_3	a_3	b_4	a_4	c_5	b_5	a_5	c_6	b_6	a_6	d_7	c_7	b_7	a_7	d_8	c_8	b_8	a_8
Maximum electron in orbit			2	2	6	2	6	2	10	6	2	10	6	2	14	10	6	2	14	10	6	2
1st	1	OM	1																			
	2	N	2																			
2nd	3	PN		1																		
	4	NO	2	2																		
3rd	5	Li				1																
	6	Be			1	1																
	7	B			2	1																
	8	C			3	1																
	9	N			4	1																
	10	O			5	1																
	11	F			6	1																
	12	Ne	2	2	6	2																
4th	13	Na						1														
	14	Mg					1	1														
	15	Al					2	1														
	16	Si					3	1														
	17	P					4	1-														
	18	S					5	1														
	19	Cl					6	1														
	20	A	2	2	6	2	6	2														
5th	21	K									1											
	22	Ca								1	1											
	23	Sc							1	1	1											
	24	Ti							2	1	1											
	25	V							3	1	1											
	26	Cr							4	1	1											
	27	Mn							5	1	1											
	28	Fe							6	1	1											
	29	Co							7	1	1											
	30	Ni							8	1	1											
	31	Cu							9	1	1											
	32	Zn							10	1	1											
	33	Ga							10	2	1											
	34	Ge							10	3	1											
	35	As							10	4	1											
	36	Se							10	5	1											
	37	Br							10	6	1											
	38	Kr	2	2	6	2	6	2	10	6	2											
6th	39	Rb												1								
	40	Sr											1	1								
	41	Y										1	1	1								
	42	Zr										2	1	1								
	43	Nb										3	1	1								
	44	Mo										4	1	1								
	45	Tc										5	1	1								
	46	Ru										6	1	1								
	47	Rh										7	1	1								
	48	Pd										8	1	1								
	49	Ag										9	1	1								
	50	Cd										10	1	1								
	51	In										10	2	1								
	52	Sn										10	3	1								
	53	Sb										10	4	1								
	54	Te										10	5	1								
	55	I										10	6	1								
	56	Xe	2	2	6	2	6	2	10	6	2	10	6	2								

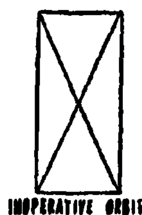


Fig. 22. Electronic structure of elements.

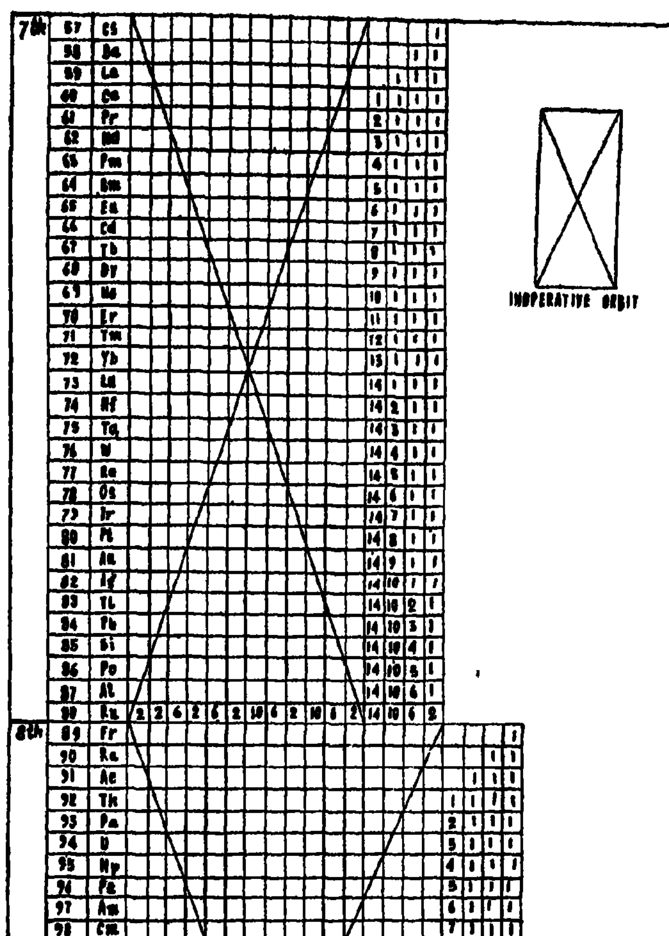


Fig. 22 (Contd.) Electronic structure of elements.

This means that with the atomic configuration remaining constant, addition of electrons in orbits can go on without limit.

Just as development of macrosphere in one direction only is relevant to us, so also are microspheric developments in one direction. Numerically, macrospheric and microspheric developments takes start from 9 square units in the configuration of symmetry consisting of 25 square units. The difference lies in the fact that the configuration in macro development varies (here increase) outward as indicated in Fig. 17(a) following the series 2, 2; 8, 8; 18, 18; 32, 32 and so on but in orbital micro development, the electrons increase in orbit as 2, 2; 2, 6; 2, 6; 2, 6, 10; 2, 6 10; 2, 6, 10, 14; 2, 6, 10, 14 and so on. On these basis the electronic structures of atoms have been drawn in Fig. 22. It may be noticed that in Fig. 22 the electrons in orbits of atomic configuration are arranged in the order as 14, 10, 6, 2, i.e., decreasing towards outer orbits.

There are certain unique and obvious features in the new arrangement.

(i) This explains why the elements Sc, Y and La possess almost identical chemical properties with rare earth group of tervalent elements which possess, in the last three columns, one electron each.

(ii) Likewise Ce and Th have one electron in each of the last four columns and though they are included in the tervalent rare earth and actinium series, they have special properties in being quadrivalent and have oxides which are highly incandescent. Again, though these two elements are tetravalent they are different from other tetravalent elements like Ti, Zr and Hf.

Section 3

Application in Thermodynamics and Specific Heats

3(a) *Nature of thermodynamic phase continuum from properties of vapour and liquid H_2O in equilibrium combination in different phases starting from H_2O as permanent gas to solid ice :*

The thermodynamic data of H_2O as permanent gas, vapour and liquid in combination as well as equilibrium combination of solid ice and supercooled liquid, particularly with respect to two

TABLE 7

Temperature °F	Space	Equilibrium Phases: H_2O as permanent gas Sp Vol.	Entropy				
1600		0.3703	1.7080	Liquid H_2O phase eliminated			
1200		0.2806	1.5742				
1000		0.2288	1.4874				
900		0.1961	1.4309				
800		0.1588	1.3508				
705·4	Vap-Liq Critical State	0 0503	1.0580				
		Vapour H_2O Sp. Vol.	Entropy	Liquid H_2O Sp. Vol.	Entropy		
705.4		0.0503	1.0580	0.0503	1.0580		
600		0 2668	1.3307	0.0236	0.8181	Solid phase eliminated	
450		1.0993	1.4793	0.0194	0.6280		
300		6.466	1.6850	0.01745	0.4869		
150		97.07	1.8685	0 .01634	0.2149		
(39.2 ?)	Solid liquid critical state	2518	2.1620	0.01602	0 0142		
32		3306	2.1877	0.01602	0.0000		
Temp. °C				Liquid H_2O super-cooled Den. gm/c.c.	Entropy	Solid H_2O Sp Vol.	Entropy
0		14810	2.3297	(+4) 1.0000 (0°C) 0.99987		0.01742	−0.3244
−50		249600	2.6028	(−4) 0.99945		0.01785	−0.3758
−150		985200	2.9503	(−8) 0.99869 −(10°C) 0.99815		0.01720	−0.4266

Specific Vol. as Cft/lb Entropy as BTU/lb/°R

Data above 705.4°F are at constant pressure of 3206 2 lb/sq inch abs.

specific properties, namely, specific volume and entropy have been presented in Table 7. The solid/liquid critical state has been assumed near about 39.2°F or 4°C at which the liquid phase has the maximum density. No data is available about the property of ice between 0°C and 4°C. There must be appearance of solid ice phase between 4°C and 0°C.

At 705.4°F, the vapour/liquid critical state, the specific volume and entropy of both vapour and liquid are identical. At this state, liquid phase loses its identity from vapour phase. At temperatures above this critical state, vapour and liquid phase cannot exist, only H_2O as permanent gas can exist. Below this critical state, vapour and liquid co-exist in equilibrium combination. At 705.4°F, H_2O as permanent gas arrives at its least specific volume, from 0.3703 at 1600°F to 0.0503 and the entropy changes from 1.7080 at 1600°F to 1.0580. The properties of vapour phase and liquid phase in equilibrium combination, below their critical state, vary in opposite directions. The specific volume and entropy progressively increase in the vapour phase with decrease in temperature while in the liquid phase in combination, they change in opposite direction. The liquid H_2O phase starting with 0.0503 as specific volume and 1.0580 as entropy at 705.4°F progressively decreases to 0.01602 specific volume and 0 entropy at 32°F whereas in the vapour phase the specific volume starts with 0.0503 at 705.4°F and increases to 3306 at 32°F.

Below the solid/liquid critical state, the density of H_2O in the super-cooled liquid phase decreases from 1 at 4°C to 0.99815 at -10°C i.e., the increase of sp. vol. of super-cooled liquid with temperature occurs just in the same way as that of H_2O in vapour phase does with lowering of temperature in its phase combination with liquid above the solid-liquid critical state. The properties of solid H_2O in equilibrium with super-cooled liquid H_2O below solid-liquid critical state progressively change from 0.1742 in specific volume and −0.3244 in entropy at 0°C to 0.01720 in specific volume and −0.4266 in entropy at −150°C. It can be seen in this phase combination also that the super-cooled liquid phase progressively increases in specific volume while the solid phase progressively decreases in specific volume. The data for entropy in the liquid phase is not available but the nature of change of properties of phase combinations of H_2O which occur through the vapour/liquid critical state, identical

nature of change of properties also should occur through the solid-liquid critical state. It is significant that the liquid phase above the solid/liquid critical state possesses opposite characteristics of liquid phase below the solid/liquid critical state. The maximum density is at 4°C. Liquid phase below the solid/liquid critical state is not the identical liquid above the solid-liquid critical state. Above the solid/liquid critical state, 4°C, the phase of H_2O as ice cannot permanently exist just as liquid phase above the vapour-liquid critical state of 705.4°F cannot exist. Thus, the two critical states are similar in nature.

3(b) *Brief description of the nature of continuum :*

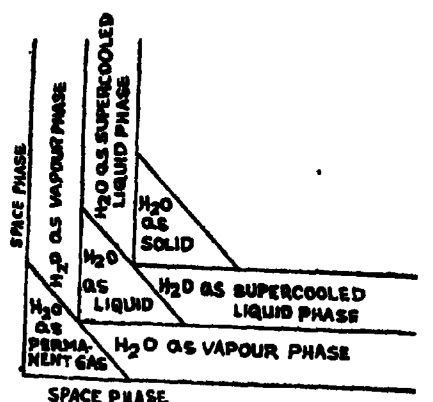
The essence of the whole picture of the nature of continuum in the evolutionary context is like progressive changes of twin phase combinations through critical states one after the other with respect to a change of magnitude of a critical dimension like critical temperature, velocity of light etc.

H_2O as permanent gas, vapour and liquid phases at vapour/liquid critical state of 705.4°F is in such a state of equilibrium that none of the phases is distinguishable. The critical state is an abstract state of existence wherefrom phenomenal nature starts. Starting from a temperature higher than the critical, as the temperature is progressively lowered down to the critical temperature, the permanent gas density progressively increases, till it becomes maximum at the critical state. Just below the critical temperature permanent gas becomes vapour in its continuity, having the maximum density and a new phase (liquid) with least density appears with which vapour is in equilibrium combination. The two phases in equilibrium combination possess opposite properties. With lowering of temperature, one phase (liquid H_2O) increases in intensive properties and the vapour decreases in intensive properties till the two in combination arrive at a *temperature state* where condensed phase increases to maximum intensity and the uncondensed phase, vapour, arrives at the minimum intensity. This temperature state is the second critical state wherefrom one phase (liquid) with maximum intensity transits in continuity to a phase of super-cooled liquid H_2O with maximum intensity and a new phase (ice) is generated in the new twin combination.

3(c) *Similarity between thermodynamic continuum and numerical continuum :*

The continuum of thermodynamic phases has been qualitatively shown in Fig. 23 which follows the same pattern as in the case of numerical continuum in Fig. 24.

Numerical continuum of fundamental unit and the digits in combination have been explained in Figs. 6, 7, 8 and 9. The ultimate fundamental is ONE. The digits vary from 1 to 9 within the frame work of ONE. The unit and the digits in combination make the different frames of phases of



Evolution of Thermodynamic Phase Continuum of H_2O.

Fig. 23

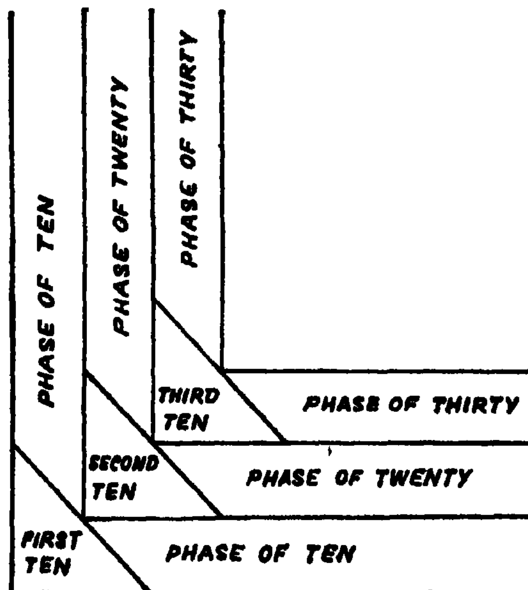


Fig. 24

numbers from 1 to 10, 11 to 20, 21 to 30 etc. The states 10, 20, 30 etc. are numerical critical states as shown in Figs. 8 and 9. The nature of association is obvious from the figure. The critical states through which the numerical phases change from previous to next are similar to the thermodynamic critical states.

The thermodynamic data of H_2O, available in Table 7 covering approximately three zones of phase combinations and two critical states, are in conformity with the configuration of symmetry of phase continuum.*

* ("Science Based on Symmetry," Chapter. 1 for detailed analysis)

TABLE 8—THERMODYNAMIC DATA OF H_2O ON TEMPERATURE, Sp. VOLUME, PRESSURE, ENTROPY, DENSITY AND HEAT OF VAPORIZATION etc., BETWEEN THE TWO CRITICAL STATES : 39.2°F AND 705.4°F (PERRY, HAND BOOK AND HODGMAN, HAND BOOK)

Temp. °F	Vap. pressure (abs) lb/sq. inch	Specific volume Liquid cft/lb	Specific volume Vapour cft/lb	Heat of vapourization BTU/lb	Entropy Liquid BTU/lb/R°	Entropy Vapour BTU/lb/R°	Density Liquid lb/cft	Density Vapour lb/cft
39.2	0.1217	0.01602	2518	1071.95	0.0162	2.1597	62 5	0.000397
50	0.1781	0.01603	1703.2	1065.63	0.0361	2.1264	–	–
100	0.9492	0.01613	350.4	1037.23	0.1295	1.9826	62.00 (at 100 4°F)	0.002884 (at 100.4°F)
200	11.526	0.01663	33.64	977.91	0.2938	1.7762	60.1	0.03
300	67.013	0.01743	6.466	909.11	0.4369	1.6350	57.47 (at 300.2°F)	0.1552 (at 300.2°F)
400	247.3	0 01864	1.8633	826.03	0.5664	1.5272	53.28 (at 410°F)	0.598 (at 410°F)
500	680.8	0.0204	0.6749	773.9	0.6887	1.4325	49.02	1.486
600	1542.9	0.0236	0.2668	548.5	0.8131	1.3307	42.37	3.746
700	3093.7	0.0369	0.0761	172.0	0.9905	1.1389	27.1	13.14
705.4	3206.7	0.0503	0.0508	0	1.0580	1.0580	19.88	19.68

3(d) *Variations of thermodynamic properties :*

Following the principle enunciated in Section 1(f) it is intended to verify the validity of the four pairs of forms of transformations listed in Table 5 by adopting various changes in thermodynamic properties of H_2O with respect to change in temperature. Established data of different thermodynamic properties of H_2O between solid/liquid critical state at 39.2°F and vapour/liquid critical state at 705.4°F have been listed in Table 8.

Let $100 = C_1 \Delta T_C = C_2 \Delta P_C = C_3 \Delta D_C = C_4 \Delta S_C = C_5 \Delta Q_C = C_6 \Delta E_C$ etc. in which ΔT, ΔP, ΔS, ΔQ, ΔD and ΔE are changes in temperature, pressure, density, entropy, heat of vapourisation and energy intensity in vapour phase and ΔT_C, ΔP_C, etc. are their critical values respectively. The following procedure has been adopted to work out the various changes of properties with respect to the yard-stick of temperature.

Suppose we want to study the variation of changes of vapour pressure ΔP and heat of vaporization ΔQ with respect to changes of temperature ΔT.

(a) Take a square configuration of 100 units × 100 units.

(b) Let the dimension temperature be taken, in terms of which relationships of changes of different properties will be studied. It should be emphasised that variation of those properties which undergo changes between the two critical states should be taken into consideration. That part of the properties which do not undergo change should be eliminated.

(c) Calculate the change in temperature between the two critical states. Let ΔT_C be the change in temperature between the two critical states. Let this temperature change ΔT_C be equal to 100 units of the side of the square configuration. The ΔT changes in temperature at lower levels will be calculated as follows : $\frac{100}{\Delta T_C} \times \Delta T$ units of side of this square.

(d) Let ΔQ_C be the critical change in latent heat of vapourization between the two critical states. The ΔQ at different temperature levels will be given by $\frac{100}{\Delta Q_C} \times \Delta Q$ units.

(e) Similarly ΔP will be given by $\frac{100}{\Delta P_C} \times \Delta P$ units.

(f) Plot ΔT units along the vertical axis AY in Fig. 25.

(g) Plot ΔQ units along the X-axis from AY towards XB at different temperature levels.

(h) Plot ΔP units from XB towards AY at different temperature levels.

From Fig. 25 we get

$$\frac{100}{\Delta Q_c} \times \Delta Q = \sqrt{\left(\frac{\Delta T_c}{\Delta T_c} \times 100\right)^2 - \left(\frac{\Delta T}{\Delta T_c} \times 100\right)^2}$$

$$= 100\sqrt{\frac{\Delta T_c^2 - \Delta T^2}{\Delta T_c^2}}$$

$$\text{or, } \frac{\Delta Q}{\Delta Q_c} = \sqrt{\frac{\Delta T_c^2 - \Delta T^2}{\Delta T_c^2}} \quad \text{... Eq. 5.}$$

Similarly,

$$\Delta P \times \frac{100}{\Delta P_c} = \frac{\Delta T_c}{\Delta T_c} \times 100 - 100\sqrt{\frac{\Delta T_c^2 - \Delta T^2}{\Delta T_c^2}}$$

$$\text{or, } \frac{\Delta P}{\Delta P_c} = 1 - \sqrt{\frac{\Delta T_c^2 - \Delta T}{\Delta T_c^2}} \quad \text{Eq. 6.}$$

These transformation equations have the same forms as i(a) and i(b) in Table 5. The Eq. 5 has the form of Lorentz transformation for length (space) contraction and Eq. 6 is the present approach to time dilation.

The above equations can be written in terms of reduced states of the different dimensions.

$$\text{Thus } \Delta Q_r = \sqrt{1 - \Delta T_r} \quad \text{.. Eq. 7.}$$

$$\text{and } \Delta P_r = 1 - \sqrt{1 - \Delta T_r} \quad \text{... Eq. 8.}$$

These can also be expressed in the forms :

$$C_5 \Delta Q = C_1 \sqrt{\Delta T_c^2 - \Delta T^2} \quad \text{... Eq. 9.}$$

$$\text{and } C_2 \Delta P = C_1 \{\Delta T_c - \sqrt{\Delta T_c^2 - \Delta T^2}\} \quad \text{... Eq. 10.}$$

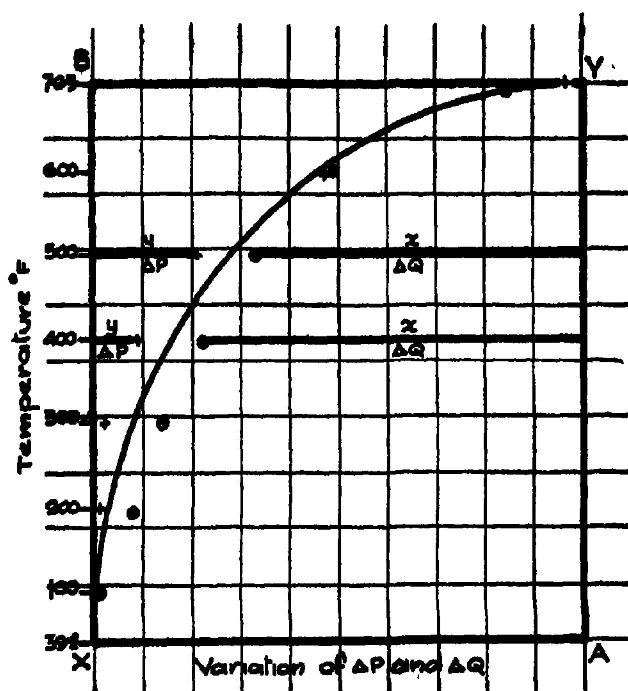


Fig. 25

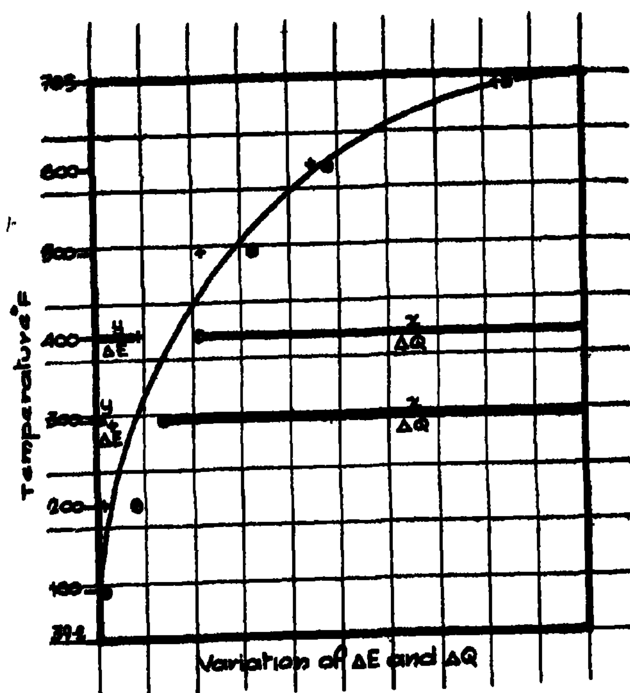


Fig. 26

The relationship of $\frac{\Delta P}{\Delta T}$ would be given by

$$\frac{\frac{100\times\Delta P}{\Delta P_c}}{\frac{100}{\Delta T_c}\times\Delta T}=\frac{\frac{100}{\Delta T_c}\left(\Delta T_c-\sqrt{\Delta T_c^2-\Delta T^2}\right)}{\frac{100}{\Delta T_c}\times\Delta T}$$

or, $$\frac{\Delta P}{\Delta T}=\frac{\Delta P_c}{\Delta T_c}\times\frac{1}{\Delta T}\times\left(\Delta T_c-\sqrt{\Delta T_c^2-\Delta T^2}\right)$$

... Eq. 11.

Changes of heat of vapourization ΔQ and changes in energy intensity ΔE of vapour phase have been plotted against changes of temperature in Fig. 26

$$\Delta EC_s = C_1(\Delta T_c - \sqrt{\Delta T_c^2 - \Delta T^2}) \quad \ldots \text{ Eq. 12.}$$

$$\frac{\Delta EC_s}{C_1} = (\Delta T_c - \sqrt{\Delta T_c^2 - \Delta T^2})$$

Substituting in equation 11 we have,

$$\frac{\Delta P}{\Delta T} = \frac{\Delta P_c}{\Delta T_c \, \Delta T} \times \Delta E \times \frac{C_s}{C_1} \quad \ldots \text{ Eq. 13.}$$

From this we get

$$\frac{\Delta P_r}{\Delta T_r} = \frac{C_s}{C_1 \Delta T} \times \Delta E \quad \ldots \text{ Eq. 14.}$$

Putting the values of C_s and C_1

$$\frac{\Delta P_r}{\Delta T_r} = \frac{\Delta E}{\Delta E_c \, \Delta T_r} \quad \ldots \text{ Eq. 15.}$$

Since $\Delta E = \frac{\Delta Q}{\Delta(V_v - V_1)}$ and $\Delta E_c = \frac{\Delta Q_c}{\Delta(V_v - V_1)_c}$

we finally have

$$\frac{\Delta P_r}{\Delta T_r} = \frac{\Delta Q_r}{\Delta T_r \, \Delta(V_v - V_1)_r} \quad \ldots \text{ Eq. 16.}$$

This has the form of Clausius Clapeyron's famous equation correlating changes of vapour pressure with changes of temperature and latent heat of vapourization all expressed in their reduced states.

3(e) *Changes of entropy of vapour and liquid phases of H_2O :*

Following the same procedure, variation of entropy changes ΔS_v and ΔS_1 in the vapour and liquid phases respectively have been calculated and the data have been plotted in Fig. 27. The figure shows that the entropy changes vary between the two critical states maintaining conservation.

Thus, $\Delta S_v = (\Delta T_c - \Delta T)$ and $\Delta S_1 =$

$\Delta T_c - (\Delta T_c - \Delta T)$ and further $\frac{\Delta S_v}{\Delta S_{v_c}} = \frac{(\Delta T_c - \Delta T)}{\Delta T_c}$

$$\text{and } \frac{\Delta S_1}{\Delta S_{1_c}} = 1 - \frac{(\Delta T_c - \Delta T)}{\Delta T_c} \quad \ldots \text{ Eq. 17.}$$

The forms of transformations follow iii(a) and iii(b) in Table 5.

A significant point may be noted is that variation of entropy changes in the two opposite phases in equilibrium combination maintaining conservation, goes against the famous postulate of Clausius namely, "Energy of the universe is constant, entropy tends to maximum". The relationship shows that entropy does maintain conservation.

3(f) *Changes of specific heats :* These are much more complicated than variations of changes of thermodynamic properties with respect to changes in temperatures. Some of the factors contributing to the apparent anomalies and complications are :

(a) Many substances vary in specific volumes while in equilibrium existence comprising different phase combinations.

(b) It may not be known in what phase a substance belongs to. Whether it is uncondensed or the condensed phase. Because in the present approach if a substance is a

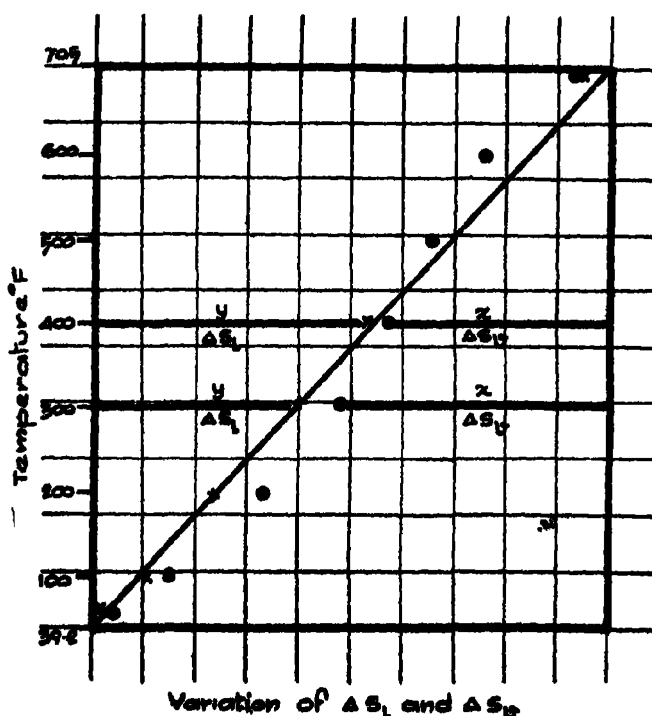


Fig. 27

condensed phase its specific heat should increase with temperature and if uncondensed, specific heat should decrease with temperature. For example, specific heats of super-cooled liquid H_2O, which is a uncondensed phase, decrease with temperature and specific heats of solid ice which is condensed phase increase with temperature.

(c) A substance may be a mixture of both phases like a solid solution. Specific heat of solid Hg upto its melting point −36.7°C increases with temperature, behaving as a condensed phase. But at temperature above −36.7°C, the specific heats decrease with temperature. Liquid Hg is behaving here as uncondensed phase. Similarly, data on H_2O from 0°C to 34°C are anomalous. Specific heat of solid Pb from −270°C upto 360°C increases with temperature behaving like condensed phase. There are many other cases which require further study.

We shall deal with the variations in changes of specific heats of aluminium with changes of temperature following the same procedure. We are presenting in Fig. 28 the variation of changes in specific heats of aluminium with changes of temperature. Einstein and Debye did extensive work on this and Debye's formula has been found to be near to the experimental data. Applying our method we got the following relationship from Fig. 28.

$$\frac{\Delta h}{\Delta h_0} = \sqrt{\frac{\Delta T_0^2 - (\Delta T_0 - \Delta T)^2}{\Delta T_0^2}} \quad \ldots \text{ Eq. 18.}$$

where Δh is variable specific heats at different temperature levels and Δh_0 is critical specific heat at 660°C which is the melting point.

It should be noted that the form of transformation in this case is ii(a) of Table 5. This form of transformation is exactly opposite of Lorentz form.

3(g) *Variation of specific heats of ice with temperature :*

Variation in changes of specific heats of ice with changes of temperature have been plotted in Fig. 29. The relationship of the form of transformation is expressed as :

$$\frac{\Delta h}{\Delta h_0} = \frac{\Delta T_0 - (\Delta T_0 - \Delta T)}{\Delta T_0} \quad \ldots \text{ Eq. 19.}$$

This form corresponds to iv(a) in Table 5.

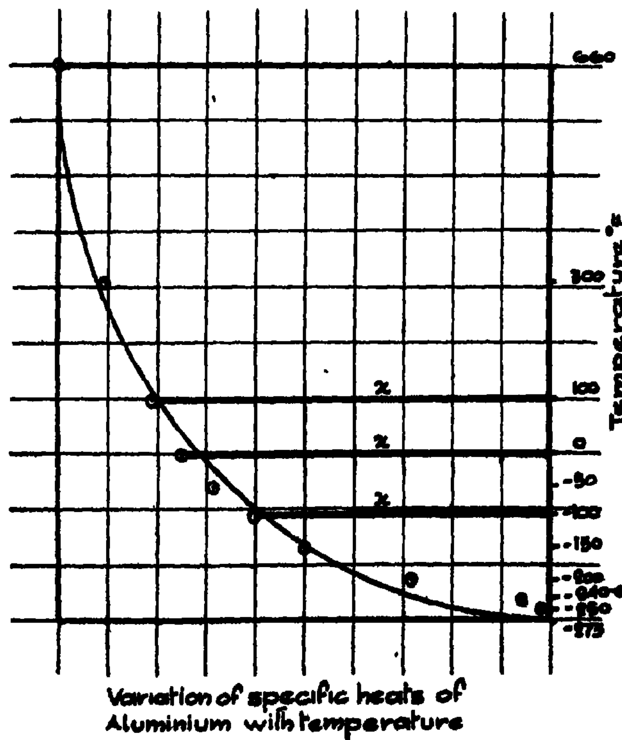


Fig. 28

$$\Delta EC_e = C_1(\Delta T_e - \sqrt{\Delta T_e^2 - \Delta T^2}) \quad \dots \text{Eq. 12.}$$

$$\frac{\Delta EC_e}{C_1} = (\Delta T_e - \sqrt{\Delta T_e^2 - \Delta T^2})$$

Substituting in equation 11 we have,

$$\frac{\Delta P}{\Delta T} = \frac{\Delta P_e}{\Delta T_e \, \Delta T} \times \Delta E \times \frac{C_e}{C_1} \quad \dots \text{Eq. 13.}$$

From this we get

$$\frac{\Delta P_r}{\Delta T_r} = \frac{C_e}{C_1 \Delta T} \times \Delta E \quad \dots \text{Eq. 14.}$$

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Following the same procedure, variation of entropy changes ΔS_v and ΔS_1 in the vapour and liquid phases respectively have been calculated and the data have been plotted in Fig. 27. The figure shows that the entropy changes vary between the two critical states maintaining conservation.

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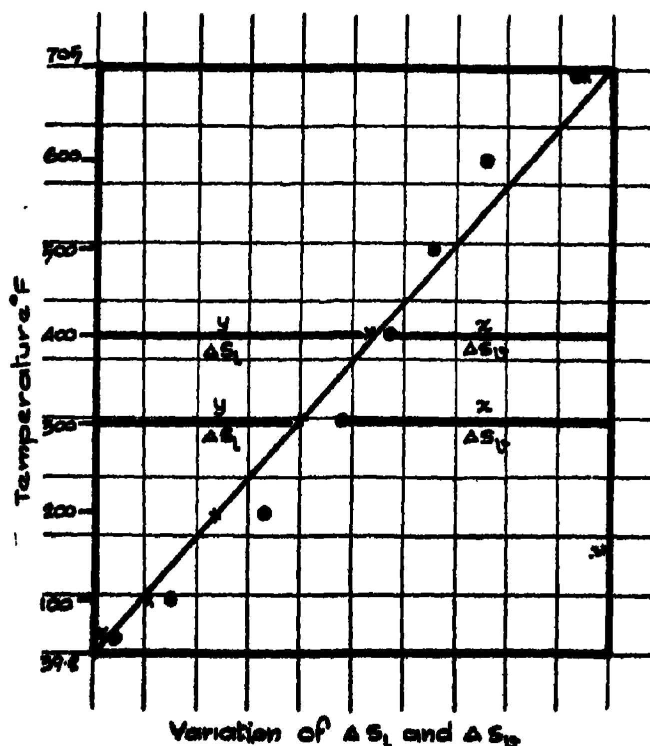


Fig. 27

condensed phase its specific heat should increase with temperature and if uncondensed, specific heat should decrease with temperature. For example, specific heats of super-cooled liquid H_2O, which is a uncondensed phase, decrease with temperature and specific heats of solid ice which is condensed phase increase with temperature.

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We shall deal with the variations in changes of specific heats of aluminium with changes of temperature following the same procedure. We are presenting in Fig. 28 the variation of changes in specific heats of aluminium with changes of temperature. Einstein and Debye did extensive work on this and Debye's formula has been found to be near to the experimental data. Applying our method we got the following relationship from Fig. 28.

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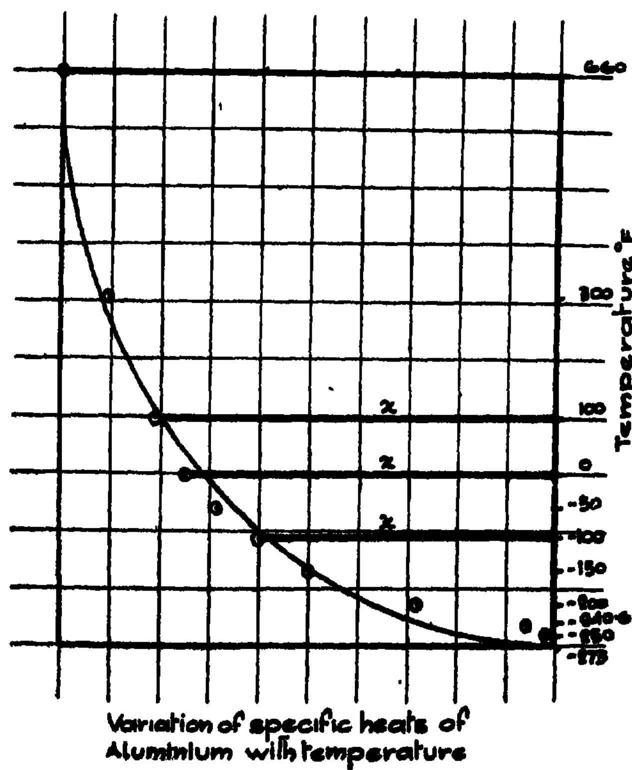
It should be noted that the form of transformation in this case is ii(a) of Table 5. This form of transformation is exactly opposite of Lorentz form.

3(g) *Variation of specific heats of ice with temperature :*

Variation in changes of specific heats of ice with changes of temperature have been plotted in Fig. 29. The relationship of the form of transformation is expressed as :

$$\frac{\Delta h}{\Delta h_0} = \frac{\Delta T_0 - (\Delta T_0 - \Delta T)}{\Delta T_0} \quad \ldots \text{ Eq. 19.}$$

This form corresponds to iv(a) in Table 5.



Variation of specific heats of Aluminium with temperature

Fig. 28

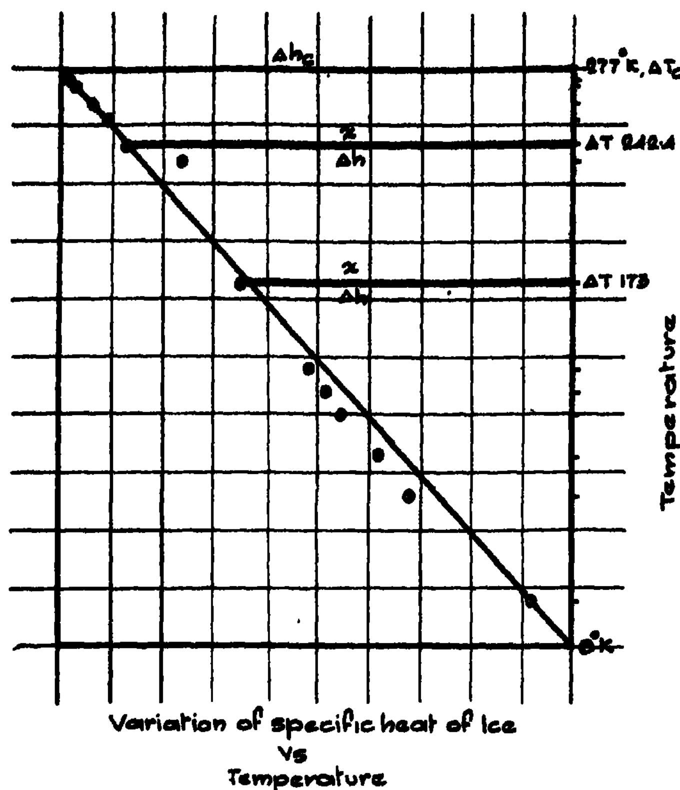


Fig. 29

Section 4

Application in Space and Time Transformations. Analysis of Motion along Circular path in a Plane

4(a) *Velocity components and their space and time contents along X and Y axes :*

Consider the velocity components along X and Y axes of an object in uniform motion along circular path in a plane. Let A be the starting position. In Fig. 30 the object moves in uniform motion along AA_1A_2BCD etc.

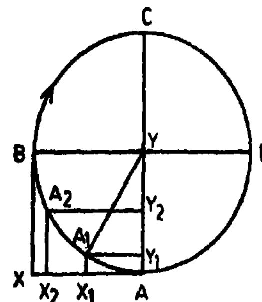


Fig. 30. Components along X and Y axes of uniform motion along circular path.

While the object is in uniform motion, at any instant in its own path, the space covered and time taken are intimately associated. Space and time move simultaneously with the object at various instants and positions in its own path. Thus space and time are inseparable with respect to the object in motion. In other words the total path described by the object is a measure not only of space but also equally of time. Both time and space are expressed in terms of space.

Let us divide the circular path between A and B in Fig. 30 into 3 equal parts viz., AA_1, A_1A_2, A_2B. Time and space for each of these three equal parts are identical.

It is intended to bring the space aspect as well as the time aspect in the configuration as they would be realised along the X and Y axes. As the motion (velocity) is uniform in circular path, space covered divided by time taken (which is velocity) from A to A_1, A_1 to A_2 and A_2 to B are identical along the circular path of the motion along AA_1A_2B. But their components along X axis would be AX_1, X_1X_2 and X_2X. Similarly along Y axis the corresponding components would be AY_1, Y_1Y_2 and Y_2Y. It may be seen that the magnitudes of the components along the two axes vary in opposite manner. The velocity component along X axis progressively decreases in proportion to AX_1, X_1X_2 and X_2X respectively. Along the X axis magnitude of space of each component progressively decreases while magnitude of time progressively increases (because the velocity component L/T progressively decreases along X axis). Similarly along Y axis magnitude of

space component progressively increases and magnitude of time component progressively decreases (because velocity component L/T progressively increases along Y axis). This should be expected because X and Y axes are opposites.

Following this method, one can visualise the consequences on space and time configurations and the relationships between the velocity components along X and Y axes for the complete motion of the object along the circular path.

For example Figs. 31(a) and (b) reveal the velocity components along X axis and Y axis respectively of the motion along the complete circular path. These velocity components have

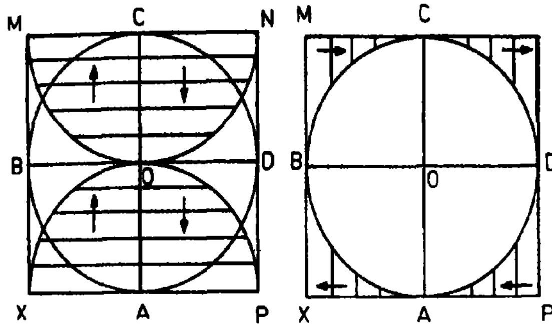


Fig. 31(a). Velocity of components along X axis for the complete circular path of motion.

Fig 31(b). Velocity of components of Y axis for the complete circular path of motion.

been further split into space content and time contents of velocity components of motion along the complete path. Fig. 32 shows space and time contents of velocity components along X axis and Fig. 33 shows space and time contents of velocity components along Y axis. Rearranging, the total

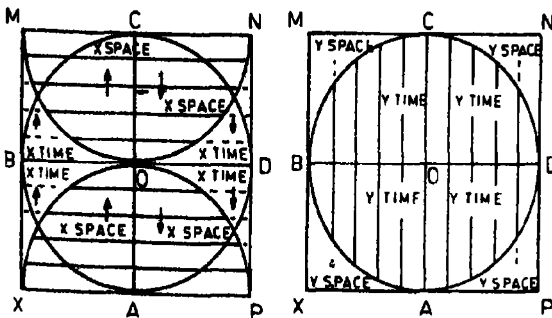


Fig. 32

Fig. 33. Space and time contents of velocity components along Y axis.

space contents of X and Y axes into one configuration is shown in Fig. 34(a) and total time contents along X and Y axes in Fig. 34(b).

The above geometrical analysis establishes conservation of velocity components. It also establishes not only conservation of space content

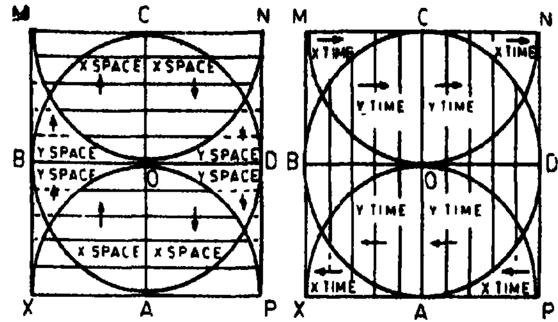


Fig. 34(a). Variation of X space and Y space along X axis.

Fig. 34(b). Variation of X time and Y time along Y axis.

and time content but also space time conservation, equivalence and interchangeability of space and time in the universal context. Another important point is that both space and time can dilate and contract depending on the course of motion. And all the space and time contents, of all varying velocity components along X and Y axes, undergo dilation or contraction according to the following forms of transformation equations :

$$\text{(a)}\quad l_2 = l_1\sqrt{\frac{c^2 - v^2}{c^2}} \text{ and } t_2 = t_1\left[1 - \sqrt{\frac{c^2 - v^2}{c^2}}\right]$$

$$\text{and (b)}\quad l_2 = l_1\sqrt{\frac{c^2 - (c-v)^2}{c^2}}$$

$$\text{and } t_2 = t_1\left[1 - \sqrt{\frac{c^2 - (c-v)^2}{c^2}}\right]$$

These forms have already been listed in Table 5.*

4(b) *Geometrical configuration of Lorentz transformation : space can contract and dilate ; so also time :*

The most important aspect of Lorentz's transformation is the factor $\sqrt{\frac{c^2 - v^2}{c^2}}$. When $v=0$, the factor becomes unity, and when $v=c$, the factor becomes zero. These conditions are satisfied if the three dimensions viz., c, v and $\sqrt{(c^2 - v^2)}$ form the three sides of a right-angled triangle in which v varies, $\sqrt{c^2 - v^2}$ varies and c remains constant as hypotenuse [Fig. 35(a)].

In Fig. 35(a) v varies along Y axis. Its value at A is zero. $\sqrt{(c^2 - v^2)}$ varies along X axis which ranges in values from XA, where $v=0$, to zero at Y, where $v=c$.

Let a rod of length l_1, in Fig. 35(b), be at rest along AX. This rod at velocity v will be l_2 following the relationship $l_2/l_1 = \sqrt{\frac{c^2 - v^2}{c^2}}$. When $v=0$, the length is l_1. If velocity approaches c, l_2 will be zero at Y_1.

*"Science Based on Symmetry", Chapter 5, Section XVII and XVIII for details.

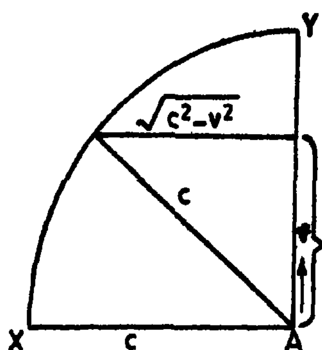


Fig. 35(a)

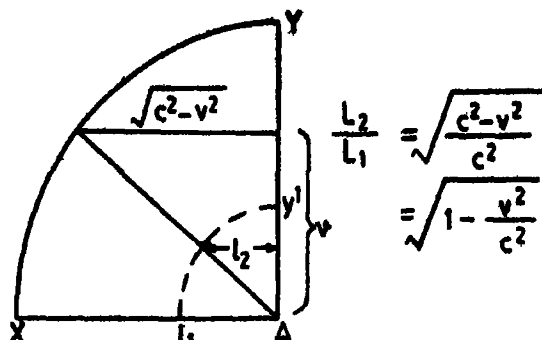


Fig. 35(b)

In order to find variation of magnitude of time, Lorentz's formula can be applied in an extended form as shown in Fig. 35(c).

In this approach if the area AXY is described by varying horizontal full lines (which are the space contents of velocity component) of magnitudes $\sqrt{c^2-v^2}$ with velocity v varying from A to Y, the horizontal dotted lines in the area XBY will be described by time contents of the velocity component.

Fig. 35(c) shows that $c-\sqrt{(c^2-v^2)}=t_2$ while the velocity v would increase from A to Y. If the velocity is equal to c=AY, the corresponding magnitude of l_1 at Y will be zero and the time magnitude will be t_1=BY. This is the form of transformation for dilation of time.

The relationship is given by $t_2=t_1\frac{(c-\sqrt{c^2-v^2})}{c}$.

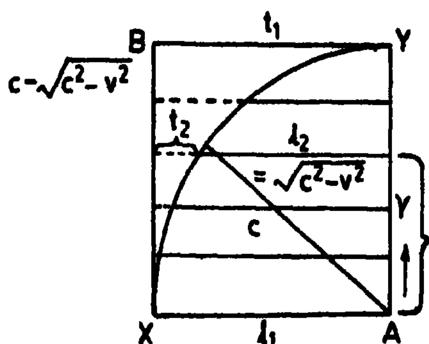


Fig. 35(c)

It should be noted that the forms of transformations of *space* and *time contraction* and *dilation* respectively follow same forms as deduced in Table 5. In the specific case under consideration space contraction and time dilation will obey the following forms:

$$l_2=l_1\sqrt{\frac{c^2-v^2}{c^2}}$$

$$t_2=t_1\frac{(c-\sqrt{c^2-v^2})}{c}$$

It must be emphasised that in the universal nature, contraction of space and dilation of time are not the only processes which work in phenomenal manifestations. There are processes in which space dilates and time contracts, following the forms of relationships, ii(a) and ii(b) in Table 5, as would be evident from Fig. 35(d) where

$$l_2=l_1\sqrt{\frac{c^2-(c-v)^2}{c^2}} \text{ and}$$

$$t_2=t_1\left(1-\sqrt{\frac{c^2-(c-v)^2}{c^2}}\right).$$

In this case space dilates and time contracts with increase of velocity.

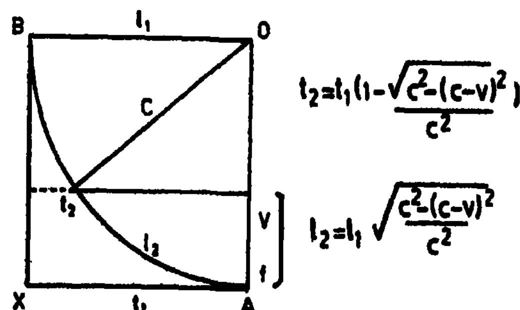


Fig. 35(d). Reverse or opposite configuration of Lorentz's transformation which could lead to time contraction and length dilation with velocity increase.

We have already shown the application of this form in variation of changes in specific heats, numerous cases of analysis of space and time contents of velocity components of uniform motion along circular path as well as matter energy wave mechanism based on symmetry in our approach.

4(c) *Relativistic mass and matter energy relationship* :

In the special theory of relativity, conventionally, the variable mass M of a body moving with velocity v is given by

$$M=\frac{m_0}{\sqrt{\frac{c^2-v^2}{c^2}}}, \text{ where } m_0 \text{ is rest mass.}$$

When $v=0$, $M=m_o$. At this state there is no kinetic mass or energy. This is a critical state, where all mass is rest mass, m_o. When $v=c$, the magnitude of M becomes infinity and m_o/M becomes zero.

But in the case of variable length l of a body with l_o as rest length the relationship is

$$\sqrt{\frac{c^2-v^2}{c^2}}=\frac{l}{l_o}$$

by applying Lorentz form of transformatinn where l is variable length and l_o is rest length.

With increasing v and decreasing value of the Lorentz factor the variable length l decreases, the limits of variations are zero and l_o. But with a variation of the value of Lorentz factor in the same direction, the limits of variation of M is m_o and infinity. Out of the eight forms of transformations, discovered in science based on symmetry, one of them, [i(a), listed in Table 5], is Lorentz transformation. These forms of transformations have been successfully applied to numerous cases employing established data, in thermodynamics, specific heats, space and time contents of motion as well as mechanism of matter energy waves (based on our approach of concept of symmetry). In no case magnitudes of any changing property increase to *infinity*. Each and every varying property shows conservation, within finite limits between critical states. It is asserted that in the context of finite manifestations in the finite universe, (within limits of $v=0$ and $v=c$) a varying property tending towards dilation or increase in magnitude cannot involve infinity. By adopting appropriate form of transformation, variation towards dilation or increase of magnitude can be up to a finite maximum limit. For example, a dimension like time can dilate by adopting the following forms of transformation :

$$\frac{t}{t_o}=1-\sqrt{\frac{c^2-v^2}{c^2}}$$

or $$\frac{t}{t_o}=\sqrt{\frac{c^2-(c-v)^2}{c^2}}$$

These show that time can dilate only up to maximum t_o. One should not forget that variable mass M is in combination with matter coming out of rest mass m_o with increasing velocity. When the two in combination vary, both should undergo variation in opposite directions and maintain conservation. In relativistic form of equation there is no matter energy conservation.

At a critical state where kinetic mass or energy is zero at zero velocity, at that state, only m_o remains. But when velocity is imparted to m_o, generated kinetic energy forms with some mass from m_o, a twin phase combination in which magnitudes of both phases must change in opposite directions with increasing v. Therefore, when M increases with velocity, m_o must decrease to maintain conservation ; m_o cannot retain its original magnitude when $v=c$. All of m_o at that critical state becomes one with the medium in which everything possess velocity c. The changes of M and m_o can vary according to any of the following forms :

(a) $M=(c-\sqrt{c^2-v^2})$ ... dilates with $v=c$.
(b) $m_o=\sqrt{c^2-v^2}$ ... contracts with $v=c$.
(c) $M=\sqrt{c^2-(c-v)^2}$ ... dilates with $v=c$.
(d) $m_o=c-\sqrt{c^2-(c-v)^2}$ ... contracts with $v=c$.
(e) $M=c-(c-v)$ ... dilates with $v=c$.
(f) $m_o=(c-v)$ ... contracts with $v=c$.
(g) $M=c-(c-v)$ ... dilates with $v=c$.
(h) $m_o=c-\{c-(c-v)\}$ ... contracts with $v=c$.

4(d) *Relationship in matter and energy variation in vapour and liquid equilibrium of H_2O with temperature :*

Established data on equilibrium variation of kinetic energy and potential energy, kinetic mass and potential mass with velocity or temperature between two critical states as such are not available to demonstrate matter/energy variation in our approach. We can, however, test our hypothesis on energy/matter variation in vapour and liquid in equilibrium between two critical temperature states from available data of H_2O.

We have to first ascertain what are the matter and energy significances of vapour and liquid phases. Energy significance as BTU/cft. of vapour phase can be represented by $E=\frac{Q}{v_o-v_1}$, where Q, v_o and v_1 are heat of vapourisation, Sp. vol. of vapour and Sp. vol. of liquid respectively. Similarly, matter significance as density d of liquid is $\frac{\text{lb}}{\text{cft}}$. The values of ΔE and Δd have been presented in Table 9.

We can examine from these the variation of energy of vapour with matter of liquid, since both the variables have a common denominator.

In terms of the critical maximum changes of these properties, namely, ΔT_c, ΔE_c and Δd_c, between the two critical states the values of ΔE and Δd at different temperature levels have been presented in Table 9.

TABLE 9

Temperature level °F	ΔE BTU/cft. of vapour	Δd lb/cft. of liquid	In terms of numbers of units of side of 100² ΔE	Δd
39.2	0	42.52	0	100
50	0.0006	—	0.01	—
100	2.540	42.12 (100.4°F)	0.50	98.8 (100.4°F)
200	28.6	40.22	0.59	94.5
300	140.5	37.59 (300.2°F)	2.7	88.2 (300.2°F)
400	447.4	33.40 (410°F)	8.8	78.4 (410°F)
500	1091	29.14	21.4	68.4
600	2255	22.49	44.3	52 8
700	4887	7.22	86.4	17
705.4	5090	0	100	0

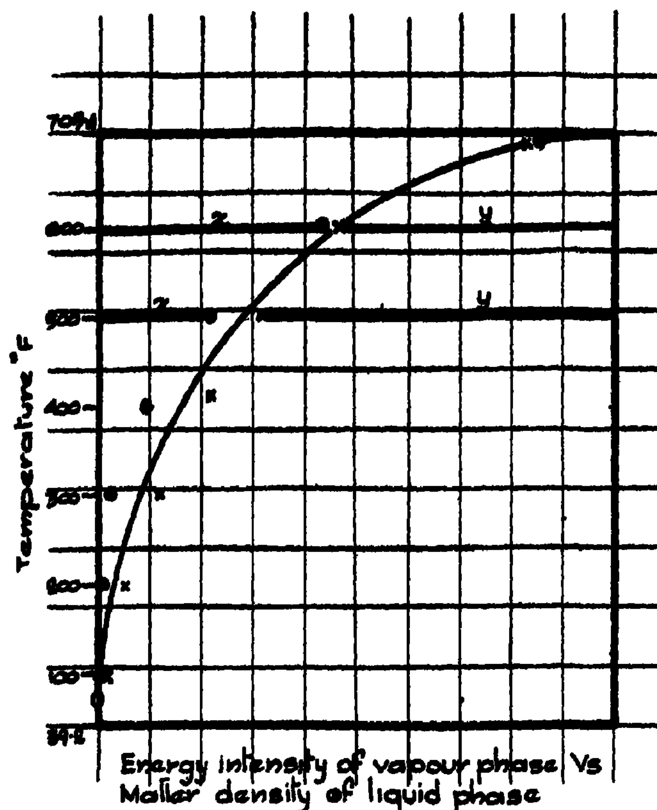


Fig. 36

The values of ΔE and Δd in terms of units of side of 100^2 have been presented in Table 9 and plotted at different temperature levels in Fig. 36, which gives the forms of transformation relationships for

$$\frac{\Delta d}{\Delta d_0}=\sqrt{\frac{\Delta T_0^2-\Delta T^2}{\Delta T_0^2}}$$

and $$\frac{\Delta E}{\Delta E_0}=1-\sqrt{\frac{\Delta T_0^2-\Delta T^2}{\Delta T_0^2}}.$$

It may be seen that as expected, the relative variations of the changes of Δd and ΔE take place in opposite directions between the two critical states maintaining matter-energy conversation.

Section 5

Mechanism of Catalytic Chemical Reaction

Dynamic aspects :

In all changes involved in nature whether it is a chemical reaction or a phenomenal manifestation, for *equilibrium existence* two opposite components like condensed and uncondensed phases are necessary for generating resultant equilibrium. For example, an observed crystalline structure must have within it a component configuration vibrating between opposite phases so that the observed or perceived configuration of the crystalline structure is the resultant of these two opposites.

This can be illustrated by a simple example of a perceived cubic configuration, generated from a tetrahedron having its centroid position fixed, vibrating between two opposite phases (Fig. 37) ABCD and abcd, where 8 positions occupy 8 corners of a cube.

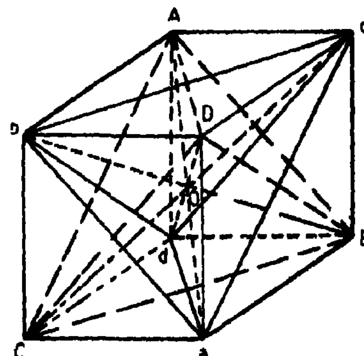


Fig. 37

Such a cubic crystal of equilibrium configuration, of course, does not have any vacant positions of the tetrahedron while vibrating between the two opposite states.

Similarly, when a tetrahedron vibrates between two opposite phases, with mid point of altitude fixed, result only six cognisable positions in the equilibrium configuration result, which appear in perception as an octahedron (Fig. 38).

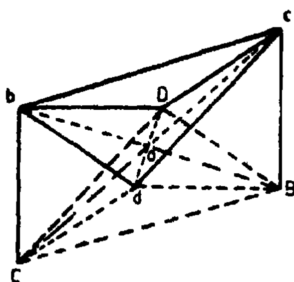


Fig. 38

The mechanism of catalytic chemical reaction has been put forward below according to this basic concept.

The entities which catalyze a reaction (catalysts) must have a configuration. The solid catalyst has a perceivable equilibrium configuration in the form of various crystalline structures. In these crystalline structures having different configuration, it may be that the perceived configuration corresponding to any crystalline structure may be only a portion of the actual equilibrium configuration in which the filled up positions are not amenable to function as catalyst while the unoccupied or unfilled or unsaturated positions can be active as catalyst.

The above illustrations provide the basis for the explanation of mechanism of catalytic reaction, particularly its dynamic aspects. It is possible that a catalytic substance is one in which an equilibrium crystalline configuration exists where all positions are not incorporated in the apparent configuration but some positions remain unoccupied or unassociated or unfilled, rendering the configuration incomplete. It is in these vacant positions that compounds as reactants are adsorbed or chemisorbed and then, because of oscillation of these positions between two opposite phases, namely reactant phase and product-phase, corresponding to condensed phase and uncondensed phase, they are oriented and transformed into products from the adsorbed reactants. To facilitate the maximum number of active positions available for the (poison free) reactants to be adsorbed, a catalyst may contain promoters, if required pretreatment like reduction, dehydration etc. may be necessary and pressure and temperature are to be adjusted to the desired level to make the vibration not only optimum for rate of reaction but also for rendering the catalyst dynamic enough to establish optimum equilibrium between adsorption and desorption. The sequences in the mechanism of a catalytic reaction would be as shown in Fig. 39.

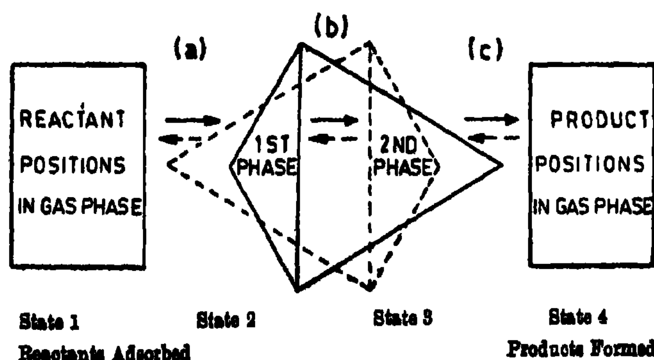
In Fig. 39 equilibrium configuration of the catalyst has been assumed to be constituted of component configuration, like a tetrahedron vibrating between two opposite phases, generating a resultant configuration like that of a cube or octahedron.

In a complete catalytic transformation process there will be three main steps of action in sequence in the direction of conversion of reactants to products :

(i) First action is conversion of the reactant positions to be adsorbed in the first phase of the catalyst configuration at suitable temperature, pressure, etc. This requires the reactant positions distributed in space to be brought to correct concentration (say by pressure adjustment) to suit distribution in the catalyst configuration in the first phase. The first action is likened to condensed phase such as liquified H_2O from vapour phase.

(ii) The second action is the change of orientation of the catalyst configuration from the first phase with reactant positions occupying the active positions to the second phase of the catalyst configuration, during which the reactants have been converted into products i.e. the reactants have undergone orientation in their combination. During this process the reactants, which were present in the first phase of the configuration associated with certain intensity of space (in this theory energy radiation is space) energy have also undergone change in the second phase, in which the products in the configuration associated with changed energy intensity of space, decide whether the reaction will be exothermic or endothermic.

(iii) The third action is the process of desorption or ejection of the product positions received from the second phase. The rate of desorption of the product positions formed in the second phase of the catalyst will be due to the difference in driving force between concentration of the product positions



State 1 Reactants Adsorbed — State 2 — State 3 — State 4 Products Formed

Fig. 39. Mechanism of catalytic reactions.

in the catalyst and their concentration in the gas phase. The third action is likened to vapourisation of liquid phase to vapour phase i.e. conversion of condensed phase into uncondensed phase.

Thus all the three steps or actions described above are factors which should be controlling the reaction.

The presence of a second or third entity mixed in the catalyst has direct effect in modifying the catalyst and its performance. They may help in generation of more active positions in the first state or they may start filling up the active positions themselves in the first state. These compounds act in two opposite ways ; they may function as promoters in the former case and as poison in the latter.

It should be noted that the physical structure of a catalyst need not be simple or elementary in nature like a tetrahedron oscillating between two states giving the impression of a cube or octahedron. It can be a combination of a number of associated configurations oscillating between two opposite phases either resonating with the vibration of the main catalyst or just vibrate in opposite mode of the main catalyst and thereby stopping catalytic activity.

The most important factor in the suggested mechanism is the introduction of dynamicity between the states of chemisorption of reactants and desorption of products.

The above concepts not only render understanding of the mechanism and rate of reaction easy but also explain the effects of promoters and poisons and such other parameters as temperature, pressure and space velocity, and role of such processes as adsorption and desorption in chemical reactions. These concepts can also be utilized to explain the endothermicity or exothermicity in chemical reaction and establishing equilibrium.

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Polymeric Bipositive Metal Ion Complexes of Terephthalaldehyde *bis*-(isonicotinic acid hydrazone)

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Terephthalaldehyde *bis*-(isonicotinic acid hydrazone) (TBINH) has been synthesized by the condensation of terephthalaldehyde and isonicotinic acid hydrazide. TBINH yields complexes, $[MLX_2.xH_2O]_n$ [M=Mn(II), Co(II), Ni(II), Zn(II), Cd(II), UO_2(VI); $L=C_{20}H_{16}N_6O_2$; $X=CH_3COO^-$, NO_3^- and $x=0$, 1 or 2], on refluxing a mixture of TBINH and metal salt in DMF medium in 1 : 1 ratio. Infrared and reflectance spectra, magnetic and thermogravimetric studies indicate that the complexes are polymeric having octahedral geometry. The order of thermal stability of the polymers is : Zn>Cd>Co>Mn>UO_2>Ni.

TEREPHTHALALDEHYDE on reaction with carbazides yield Schiff bases, behaving as tetradentate coordinating ligands, which form polymeric coordination complexes[1-5]. Metal-complexes[6-13] of Schiff bases with isonicotinic acid hydrazide, with aldehydes or ketones, have been of special interest in recent years, particularly in the context of the therapeutic value of the hydrazide and hydrazone. Coordination occurs both in keto[6,13] as well as in enolic[8,11] forms of the ligands with metal ions.

In the present communication, the synthesis of Schiff base, terephthalaldehyde *bis*-(isonicotinic acid hydrazone) (TBINH) and its complexes with Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and UO_2(VI) are being described.

Experimental

Materials : Terephthalaldehyde (Koch Light) and isonicotinic acid hydrazide (Wilson Lab.) were used to synthesize the Schiff base. $Mn(CH_3COO)_2.4H_2O$, $Zn(CH_3COO)_2.2H_2O$, $Cd(CH_3COO)_2.2H_2O$ (all BDH, AnalaR), $Co(CH_3COO)_2.2H_2O$ (Sarabhai M.), $Ni(CH_3COO)_2.4H_2O$ (Veb Laborchemie) and $UO_2(NO_3)_2.6H_2O$ (E. Merck) were used. The solvents were of reagent grade.

Preparation of Schiff base (TBINH) : Ethanolic solutions of 13.35 g (0.05 mole) isonicotinic acid hydrazide and terephthalaldehyde (6.7 g; 0.025 mole) were mixed and refluxed on a water bath for 2 hr. A white crystalline solid precipitated, which was filtered after allowing to stand for 2 hr, washed successively with water, ethanol and diethylether and dried (Yield 80%). TBINH obtained is insoluble in water, ethanol, chloroform, benzene, acetone, toluene, xylene, but soluble in dilute aqueous ammonia and DMF. Found : C, 64.61 ; H, 4.23 ; N, 22.35. Calcd. for $C_{20}H_{16}N_6O_2$: C, 64.51 ; H, 4.33 ; N, 22.57%.

Preparation of metal-chelates : TBINH (0.01 mole) dissolved in DMF was gradually added to a solution of the metal salt (0.01 mole) in DMF. Metal salts which are not soluble in DMF, were first dissolved in a minimum quantity of water and DMF was then added. The precipitation was instantaneous, but the reaction mixture was refluxed at *ca* 120° for 2 to 3 hr as necessary for completion of the reaction and left overnight. The precipitated mass was filtered, washed with DMF, ethanol and ether and dried (Yield *ca* 80%).

Properties : The 1 : 1 complexes (Table 1) are air stable and insoluble in water and in common organic solvents, viz., ethanol, acetone, benzene, coloroform, nitrobenzene, DMF and DMSO.

Spectral studies : IR spectra were recorded on Beckman Infrared spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1}, DRS were obtained in the range 200-1000 nm using Carl-Zeiss spectrophotometer VSU-2.

Magnetic measurement : Magnetic susceptibility of the complexes were determined at 298°K by Faraday's method.

Thermogravimetry : TGA was done by heating the complexes upto 800° at a rate of 10° min^{-1} in air.

Results and Discussion

The analytical data of the complexes agree with the general formula-$(MLX_2.xH_2O)_n$ [where M=Mn(II), Co(II), Ni(II), Zn(II), Cd(II), UO_2(VI); $L=C_{20}H_{16}N_6O_2$; $X=CH_3COO^-$, NO_3^-; $x=0$, 1 or 2].

Mn(II), Co(II) and Ni(II) complexes are paramagnetic with the observed magnetic moment values of 5.86, 4.98 and 2.94 B.M.* respectively. Various ligand field parameters such as ν_2/ν_1, 10 D_q, B', β and β^0 have been calculated from electronic spectral data (Table 2). The magnetic moment values together with the spectral data show the octahedral geometry of the complexes.

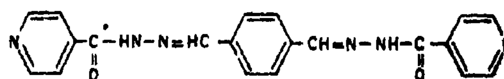
* 1B.M.=1 Bohr Magneton=9.273×10^{-24} m^2A.

TABLE 1—COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	Elemental analyses (%) Found (Calcd.)			
		M	C	H	N
$[MnLAc_2.H_2O]n$	Brownish yellow	9.26 (9.77)	50 83 (51.15)	4.07 (4.26)	14.67 (14.92)
$[CoLAc_2\ H_2O]n$	Reddish brown	9.82 (10.09)	50.63 (50.79)	4.37 (4.28)	14.14 (14.63)
$[NiLAc_2.H_2O]n$	Yellow	10.13 (10.09)	49.28 (49.28)	4.49 (4.44)	14.62 (14.86)
$[ZnLAc_2\ 2H_2O]n$	Yellow	10 83 (11 17)	48.45 (48.73)	3.98 (4.39)	14.07 (14 19)
$[CdLAc_2\ 2H_2O]n$	Yellow	17.31 (17.56)	45.13 (45 15)	3.88 (4.08)	13.42 (13.18)
$[UO_2L(NO_3)_2]n$	Yellow	30.48 (30.84)	31.81 (31 50)	2 24 (2.04)	10.18 (10.02)

$L=C_{20}H_{16}N_6O_2$, $Ac=CH_3COO^-$

The ir spectrum (Table 3, wave number in cm^{-1}) of TBINH shows characteristic absorption bands at 3240, 1640, 1290, 750 and 670 assigned to be due to N–H stretching, C=O stretching, N–H in-plane bending, N–H bending, C=O in-plane deformation and C=O out-of-plane deformation, respectively[21,22]. The bands at 1630 and 1600 are assigned to C=N and C=C stretching frequencies, respectively. The stretching vibrations due to nitrogen in pyridine ring are observed at 1490 and 1050. All these bands in the spectrum of TBINH indicate that it is present in keto form, and the proposed structure I for the Schiff base may be more likely as,



I. TBINH

A comparative study of ir spectra of TBINH and its complexes reveals the mode of coordination of the ligand. The spectra show the characteristic bands of imino and amide groups, indicating that TBINH is coordinated in keto form. In the spectra of the complexes, amide I band i.e. C=O stretching, shifts to lower frequencies, while the amide II and amide VI bands shift to higher frequencies, but amide IV remains unchanged. These observations show the coordination of keto oxygen to metal ions[23-25]. The negative shift in C=N stretching and positive shift in N–N stretching suggest that the nitrogen of the azomethine group is coordinated to metal ions[26,27].

In acetato-complexes, two bands are observed near 1440 and 1340 which may be assigned to ν(COO) and $\delta(CH_3)$ respectively[28], and in nitrato-complex bands at 1360 and 840 are assigned to stretching frequency due to nitrate group[29]. The

TABLE 2—ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF THE COMPLEXES

Complex with	Electronic Spectra Band (cm^{-1})	Assignment	ν_2/ν_1	10 Dq	B′	β	β°(%)	Geometry
Mn(II)	18,520	$^6A_{1g}\rightarrow{}^4T_{1g}(G)$	—	—	—	—	—	
	21,740	$^6A_{1g}\rightarrow{}^4T_{2g}(G)$						
	23,260	$^6A_{1g}\rightarrow{}^4E_g(G)$						Octahedral[14,15]
	26,310	$^6A_{1g}\rightarrow{}^4T_{2g}(D)$						
	29,000	$^6A_{1g}\rightarrow{}^4E_g(D)$						
Co(II)	10,000	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$	2.18	11,300	901	0 98	7.21	Octahedral[16,17]
	21,800^a	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$						
	22,220	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$						
Ni(II)	10,200	$^3A_{2g}\rightarrow{}^3T_{2g}(F)$	1 48	10,200	18,900	0.87	12.98	Octahedral[18-20]
	15,150	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$						
	27,800	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$						

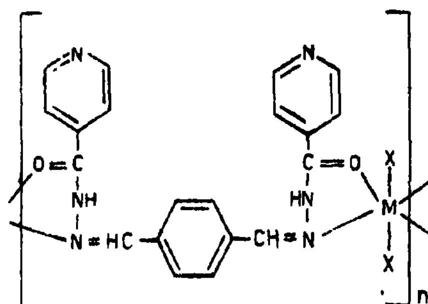
a Calculated value (Method of Lever[16]).

TABLE 3—INFRARED SPECTRA OF TBINH AND ITS COMPLEXES (Wave numbers are in cm^{-1})

TBINH	Mn(II)	Co(II)	Ni(II)	Zn(II)	Cd(II)	UO_2(VI)	Assignment
—	3400	3420	3400	3400	3450	—	O–H(H_2O) stretching
3240	3240	3240	3240	3240	3240	3240	N–H stretching
3050	3050	3050	3050	3050	3050	3050	C–H stretching
—	1665	1665	1675	1660	1660	—	H_2O deformation
1640	1590	1590	1595	1590	1590	1590	C=O stretching
1630	1620	1610	1620	1615	1620	1620	C=N stretching
1600	1600	1605	1600	1605	1605	1600	C=C (aromatic) stretching
1585	1550	1560	1560	1560	1560	1560	C–N stretching and N–H deformation
1490	1490	1495	1500	1490	1495	1490	=N–(pyridine) stretching
1285	1300	1295	1295	1300	1300	1300	N–H deformation
1050	1050	1045	1050	1045	1050	1050	=N–(pyridine) stretching
915	985	985	985	940	985	985	N–N stretching
750	750	750	750	750	750	750	C=O in-plane deformation
670	690	690	690	690	690	690	C=O out-of-plane deformation

bands observed in the regions of 3420-3380 and *ca* 1660 may be assigned to $\nu(OH)H_2O$ and $\delta(H_2O)$, respectively[26], and these indicate the presence of water in the complexes[31,32].

The metal and ligand ratio of 1 : 1 does not seem to permit a monomeric complex to exist, since the four coordinating groups of one ligand molecule cannot coordinate to a single metal ion due to steric factors and a polymeric structure II is formed by TBINH-metal linkages.



II. M=Mn(II), Co(II), Ni(II) Zn(II), Cd(II), $UO_2(VI)$ X=OH_2, OOC^-, NO_3^-.

The thermogravimetric analysis data (Table 4) of the complexes reveal that the rate of percentage loss in weight at lower temperatures is slow. The initial slopes in the curves may be due to the volatilization of water and low molecular weight moieties present in the compounds. The weight loss upto 180° corresponds to the water content of metal-chelates. The abrupt change in weight loss points to the commencement of decomposition of the complexes. The weights of the residue correspond to the formation of oxide of the respective metal. The order of thermal stability of the polymers is : Zn (420°) > Cd(400°) > Co(380°) > Mn(330°) > UO_2(320°) > Ni(300°).

TABLE 4 – THERMAL STABILITY OF THE COMPLEXES

Complex with	% weight loss of H_2O at 100-180°		Temperature °C		% weight of residue	
	Found	Calcd.	Commencement of decomposition	Completion of decomposition	Found	Calcd. for oxide
Mn(II)	3.54	3.19[a]	330	660	16.80	15 08
Co(II)	3.36	3.18[a]	380	780	15.78	14.65
Ni(II)	5.66	6.15[a]	300	520	12.27	12.87
Zn(II)	5 93	6.09[b]	420	600	14 56	13 70
Cd(II)	5.48	5.65[b]	400	520	22.86	20 07
UO_2(VI)	—	—	320	640	36.86	37.20

a for $1H_2O$. b for $2H_2O$.

The geometry of the ligand, and composition, insolubility and high thermal stability of the complexes indicate their polymeric nature.

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Synthesis and Characterization of Some Mixed Ligand Complexes of Ni(II) Ethylacetoacetate with Schiff Bases

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Some mixed ligand complexes of Ni(II) ethylacetoacetate with Schiff bases are synthesised and characterized by elemental analyses, magnetic, electronic and ir spectral studies. The results indicate that the complexes have near octahedral structure and the ligand is coordinated through nitrogen atom of azomethine group.

CONTINUED interest in the study of β-dicarbonyl complexes of nickel(II) appears to be mainly due to a variety of possible stereochemical configuration[1-3]. Considerable attention has been paid to the Schiff base complexes of nickel(II)[4-6], but not much work on the addition complexes of Schiff bases with β-dicarbonyl compounds of nickel(II) is reported. It was, therefore, considered worthwhile to prepare and characterize the addition complexes of *bis* (ethylacetoacetato)nickel(II) with Schiff bases derived from the reaction of vanillin with diamine or α-naphthyl amine or thiosemicarbazide. Certain spectral parameters have also been reported which helped in assigning the possible stereochemistry.

Experimental

All chemicals were of AnalaR grade. Nickel was estimated gravimetrically as dimethylglyoximate after decomposing the complex with a mixture of $H_2SO_4-HNO_3$ and nitrogen was estimated by Kjeldahl method. The elemental analyses of C and H were done by C.D.R.I., Lucknow. Magnetic moment measurements of the complexes in DMF were carried out on Gouy's magnetic balance at 300°K. The absorption spectra were taken in DMF on Carl-Zeiss VSU-2 spectrophotometer. The infrared spectra were recorded on Perkin-Elmer 521 spectrophotometer in the region 4000-400 cm^{-1} in KBr phase.

Schiff bases used were prepared by condensing vanillin with respective diamine or amine in stoichiometric quantities in ethanol and the Schiff bases obtained were recrystallized from ethanol and dried in vacuum at room temperature.

Preparation of complex [bis(*ethylacetoacetato*) (*vanillin*) *ethylenediamine*] *Nickel(II)* : Diaquo-*bis* (ethylacetoacetato) Ni(II)[7] (0.01*M*) was dissolved in benzene and to this Schiff base *bis* (vanillin) ethylenediamine (0.01*M*) in ethanol was added. No precipitation took place at room temperature. The reaction mixture was refluxed for 1 hr. The volume of the green solution was reduced to one third and the solution was left for crystallization in a desiccator for 3 to 4 days. The crystalline compound was washed several times with ether and dried *in vacuo*.

Preparation of other complexes :

The reactions of diaquo-*bis* (ethylacetoacetato) Ni(II) with other Schiff bases were similarly carried out. In case of Schiff base *bis*(vanillin) thiosemicarbazone, the compound obtained was dirty brown viscous liquid. The product was washed several times with ether and kept in the desiccator for slow crystallization. It took about 7-8 days to isolate the crystalline compound. In case of Schiff base *bis* (vanillin) benzidine, precipitation took place on mixing the reactants at room temperature. The yellow precipitate obtained was washed with ethanol-ether mixture and dried *in vacuo*. All these compounds were found soluble in coordinating solvents like dimethylsulfoxide, dimethylformamide and pyridine. They are sparingly soluble in solvents like ethanol, methanol and benzene.

Results and Discussion

The observed and calculated analytical data show close resemblance within the experimental limits (Table 1). The magnetic moments (3.0 to 3.3 B.M.) of the complexes are within the normal octahedral range of nickel(II)[8,9], suggesting the presence of two unpaired electrons and hence the complexes are spin free with octahedral stereochemistry.

The observed spectral data and the ligand field parameters are given in Table 2. Three bands have been observed in each complex in the region 8810 to 8890 cm^{-1}, 13790 to 14180 cm^{-1} and 21510 to 23700 cm^{-1}. The ground state of octahedral d^8 system is A_{2g} and the above spin allowed transitions, assuming distorted octahedral geometry[10] of the complexes, may be assigned to ${}^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$; ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ in the order of increasing energy and are labelled as ν_1, ν_2 and ν_3 respectively.

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TABLE 1—ANALYTICAL AND MAGNETIC DATA FOR SOME MIXED LIGAND Ni(II) COMPLEXES

Metal Complex	Physical state (Yield%)	%Ni Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	Melting point °C	Magnetic moment in Bohr Magneton μ_{eff}
1. $Ni(E)_2(VB)$ $Ni(C_6H_9O_3)_2(C_{28}H_{20}O_4N_2)$	Yellow crystalline, (94)	7.2 (7.64)	62.8 (62.60)	5.8 (5.51)	3.1 (3.65)	300	3.302
2. $Ni(E)_2(VP)$ $Ni(C_6H_9O_3)_2(C_{22}H_{24}O_4N)_2$	Shining red crystalline, (85)	8.1 (8.46)	58.7 (58.89)	5.4 (5.52)	3.0 (4.04)	90.95	3.250
3. $Ni(E)_2(VT)$ $Ni(C_6H_9O_3)_2(C_{17}H_{17}O_4N_3S)$	Dirty brown crystalline, (90)	8.6 (8.68)	51.0 (51.39)	5.1 (5.21)	6.9 (6.21)	90.0	3.283
4. $Ni(E)_2(VD)$ $Ni(C_6H_9O_3)_2(C_{20}H_{23}O_4N_3)$	Brick red crystalline, (80)	8.4 (8.52)	55.1 (55.83)	5.9 (6.29)	5.8 (6.10)	250 (decomposes)	3.196
5. $Ni(E)_2(VE)$ $Ni(C_6H_9O_3)_2(C_{18}H_{20}O_4N_2)$	Dark brown crystalline, (93)	8 9 (9.09)	55.8 (55.83)	5.9 (5.93)	4.0 (4.33)	148	3.010
6. $Ni(E)_2(VN)(H_2O)$ $Ni(C_6H_9O_3)_2(C_{18}H_{13}O_2N)(H_2O)$	Green crystalline, (90)	8.9 (9.58)	58.2 (58.84)	5.5 (5 76)	2.1 (2.28)	115-120	3.127

E=ethylacetoacetato ; VB=*bis*(vanillin)benzidine , VP=*bis*(vanillin)*o*-phenylenediimine , VT=*bis*(vanillin)thiosemicarbazone ; VD=*bis*(vanillin)diethylenetriimine, VE=*bis*(vanillin)ethylenediimine , VN=vanillin-α-naphthylimine.

TABLE 2—ELECTRONIC BANDS AND SPECTRAL DATA (cm^{-1})

Complexes*	ν_1	ν_2	ν_3	B	β	ν_2/ν_1	ν_3/ν_1	ν_3/ν_2	f	h_x	CFSE in K.cal/mole
1. $Ni(E)_2(VB)$	8890	13790	21510	565.5	0.54	1.55	2.42	1.56	1.00	3.33	30.67
2. $Ni(E)_2(VP)$	8850	13890	21600	570.58	0.55	1.57	2.44	1.56	1.01	3.75	30.80
3. $Ni(E)_2(VT)$	8910	14080	22730	690.7	0.66	1.60	2.58	1.61	0.99	2.83	30.25
4. $Ni(E)_2(VD)$	8890	14180	23700	751.74	0 72	1.60	2.67	1.67	0 98	2.33	30.37
5. $Ni(E)_2(VE)$	8730	13980	22620	692 86	0 67	1.60	2.59	1.62	0.98	2 74	29.98
6. $Ni(E)_2(VN)(H_2O)$	8770	14290	23750	781.3	0.75	1.63	2.71	1.66	0.99	2.08	30.10

* The abbreviations used here are the same as used in Table 1.

TABLE 3—INFRARED DATA

$Ni(E)_2(VE)$	$Ni(E)_2(VD)$	$Ni(E)_2(VP)$	$Ni(E)_2(VT)$	$Ni(E)_2(VB)$	$Ni(E)_2(VN)(H_2O)$	Assignment (Frequency cm^{-1})
3300 sbr 3210 s	3180 vw 3080 vw	3320 s 3130 m	3350 s 3260 ms	3210 ms 3140 s	3260 w 3030 w	N–H stretching vibration
1660 s	1650 sbr	1560 w	1665 s 1600 m	1665 s	1650 s	C=N stretching vibration
1585 m 1500 m 1460 m 1430 sh	1585 s 1500 s 1460 w 1430 w	1590 s 1515 sbr 1460 s 1430 m	1590 s 1490 s 1460 w 1425 w	1585 s 1500 s 1460 w 1425 w	1580 w 1500 s 1465 m 1430 m	Aromatic C=C vibration
1265 w	1285 m	1280 vw 1265 s	1285 w 1260 s	1290 w 1265 s	1260 s	C–O stretching vibration
1230 w 1155 w 1120 s 1028 m	1225 m 1150 w 1120 s 1025 m	1220 w 1205 w 1150 w 1020 s 1025 s	1215 w 1170 vw 1145 w 1120 w 1020 s	1225 w 1210 w 1170 m 1150 w 1120 m 1090 m 1060 w 1020 w	1225 w 1205 w 1170 s 1150 w 1120 m 1090 m 1060 m 1020 m	Aromatic in-plane deformation vibration
865 m 820 s	860 w 825 m	860 w 820 m	860 w 820 m	860 vw 820	855 m 820 s	–CH out-of-plane vibration
780 m 730 s	780 w 725 w	780 m 725 s	780 w 725 m	780 s 725 w	780 m 745 s 725 w	Aromatic CH out-of-plane vibration
485 m	455 vw	445 m	435 wbr	440 w	435 w	$\nu Ni-N$

* The abbreviations used here are the same as used in Table 1.

For d^8 complexes with O_h symmetry, Lever[11] observed that the configuration interaction between high spin $T_{1g}(P)$ and $T_{1g}(F)$ excited state lowers the ratio ν_2/ν_1 from the theoretical value of 1.8 to ~1.5-1.7 which is in confirmation with our experimental data supporting the distortion in octahedral symmetry. The value of the ratios ν_3/ν_1 and ν_3/ν_2 are also found within the range of the octahedral stereochemistry.

Various numerical methods suggested by Konig[12] have been used to calculate the value of B (Racah parameter). The value of B obtained by

using modified Tanabe-Sugano diagram[13] lies in close agreement with the above value.

The value of β (nephelauxetic ratio) shows a trend of covalent bonding in all the complexes. The CFSE values in all the complexes are almost the same which support the magnetic data. An inter-comparison of Dq and B values for the complexes shows that Dq increases in the sequence VN>VD>VT>VE>VP>VB in the spectrochemical series and almost in the inverse order in nephelauxetic series. The values of the crystal field parameter f is almost the same in all the complexes which may be due to no change in CFSE of the complexes. The nephelauxetic parameters for ligand varies from complex to complex which is due to substituted group in the ligand.

Infrared frequencies along with their tentative assignments are shown in Table 3. The band attributable to the intramolecular hydrogen bonded –OH has not disappeared in the complexes and phenolic C–O vibration shows negligible shift. This indicates that –OH of the ligand has not taken part in complex formation[14]. The elemental analysis supports the above statement. A strong band around 1590 cm^{-1} is assigned to the C=N stretch of the free Schiff bases and that found in the region 16?0-1670 cm^{-1} for the complexes. This frequency shift suggests the coordination through azomethine nitrogen[15].

Aromatic in-plane deformation vibration bands between 12?5 and 960 cm^{-1}, =CH out-of-plane vibration band near 860 cm^{-1} and aromatic CH out-of-plane vibration bands between 860 and 735 cm^{-1}[16] in the ligand do not resemble the ir spectra of the complexes. This is another support for complex formation.

The characteristic bands due to the C=O and C=C group of the *bis*(ethylacetoacetato) nickel(II) are found at 1632 cm^{-1} and 1527 cm^{-1}[17] respectively. The former one shifs to higher frequencies whereas the latter one shifts to lower frequencies. The bands appearing in the region 1720-1450 cm^{-1} on complexation, are difficult to assign as various bands fall in this region. However, the bands have been assigned tentatively comparing the spectra of the respective ligand.

Metal nitrogen stretching vibration also appears in the region 455-435 cm^{-1} in all the complexes. This band either does not shift or shifts slightly on complexation. Other Ni–N bands fall below the range of instrument.

Conclusion

The present paper describes the synthesis, magnetic and spectral study of high spin, near octahedral complexes of nickel(II) with Schiff bases. Emphasis is placed on calculation and accuracy of the interelectronic repulsion parameters. However, no quantum mechanical theory has been developed which would provide a quantitative basis for the nephelauxetic effect. It is believed that such attempts will not be successful until criteria on the accuracy and reliability of the parameter values determined from the spectra become available. To this end, the present paper is also an attempt like the other worker[13].

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Synthesis and Structural Studies of Some Mixed Ligand Bimetallic Tetrathiocyanato Complexes

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Bimetallic tetrathiocyanato complex having the formula $Ni(NCS)_2(PPh_3)_2Cu_2(SCN)_2$ has been synthesized and used as Lewis acid. It was reacted with a number of Lewis bases. The ligands become coordinated to nickel. The structures of these complexes are proposed on the basis of ir spectra, electronic spectra, conductance and magnetic moment values. The total softness values of Cu(I) and Ni(II) have also been evaluated and the difference used for establishing the nature of bonding in the complexes.

SEVERAL reports[1-4] have appeared on the studies of triphenylphosphine complexes with $MM'(NCS)_4$ [where M=Co, Ni; $M'=Hg^{++}$, $(Ag^+)_2$, $(Tl^+)_2$]. It was observed that when PPh_3 is linked with a metal, further linkage of the ligand to the metal is very difficult probably due to the large steric hindrance of the ligand.

This paper presents the studies of the complex of mixed ligand with a new type of bimetallic tetrathiocyanates $Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$ as Lewis acid. PPh_3 is a common ligand in all the complexes whereas the other donors are of varying basicity.

Experimental

Materials and manipulations : All the solvents were purified before use. Reagent grade hydrated nickel(II) nitrate, hydrated copper(II) sulphate, potassium bisulphite and potassium thiocyanate were used as such from fresh bottles. Triphenylphosphine(PPh_3) was used after recrystallisation from acetone. Dioxan (diox), dimethylformamide (dmf), pyridine (py), aniline (anl) and bipyridine (bipy) (B.D.H.) were purified by known methods. Phenanthroline (phen), 3-aminopyridine (3-amp), 4-aminopyridine (4-amp), 2-aminopyrimidine (ampn), urea (ua), *p*-toluidine (tol), benzidine (ben), α-naphthylamine (nap) and nicotinamide (nia) were used after recrystallisation from alcohol. $Ni(NCS)_2$ and CuSCN were prepared by known methods[5,6].

Syntheses of complexes : (i) $Cu(SCN)PPh_3$: 15 mmol solution of triphenylphosphine in acetone was added into a 15 mmol suspension of CuSCN in the same solvent and stirred for 20 hr. Solid complexes formed was filtered, washed with the solvent and dried in vacuum.

(ii) $Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$: 10 mmol of $Ni(NCS)_2$ and 20 mmol of $Cu(SCN)PPh_3$ were mixed together in ethyl acetate in a 250 ml flask and stirred for 48 hr. Greenish yellow complex, formed at the end of the reaction was filtered, washed with ethyl acetate and dried in vacuum.

(iii) $(L)_nNi(NCS)_2Cu_2(SCN)_2(PPh_3)_2$; (n=3 when L=bipy, phen, ben ; n=o when L=py, anl, nia, tol, nap, pip, 3-amp, 4-amp and ampn) : Homogeneous suspensions of 2 mmol of $Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$ in ethyl acetate were prepared in a number of 100 ml flasks. To these, solutions of different ligands were added in suitable molar ratio and stirred for 36 hr. Solid complexes formed were filtered, washed with the solvent and dried in vacuum.

(iv) $(L)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$; (n=2, L=dmf, ua) : 2 mmol of $Ni(NCS)_2$ and 4 mmol of $Cu(NCS)PPh_3$ were mixed together in ethyl acetate and stirred for 24 hr. The solution of the above legands were added in suitable molar ratio and stirred for further 18 hr. Green complexes, formed at the end of the reaction, were filtered, washed with solvent and dried in vacuum.

Elemental analyses : Nickel was estimated as nickel dimethylglyoximate, copper as cuprous thiocyanate, sulphur as barium sulphate gravimetrically. Nitrogen was estimated by Kjeldahl's method. The analytical data are presented in Table 1.

Physical measurements : The molar conductance of soluble complexes was measured in dimethylformamide with the Phillip PR-9500 conductivity bridge.

The infrared spectra in the region 4000-200 cm^{-1} were recorded as nujol mull on Perkin-Elmer-621 model spectrophotometer. Far infrared spectra in the region 500-50 cm^{-1} were recorded on Polytech FIR-30 spectrophotometer as polythylene pellets.

Electronic spectra were recorded on a Carl-Zeiss DMR-21 model spectrophotometer in the region 2500-250 nm.

TABLE 1—ANALYTICAL, MAGNETIC MOMENT AND MOLAR CONDUCTANCE DATA

Complexes	Colour	m.p. (°C)	μ_{eff} (B.M.)	%S Calcd.	%S Obs.	%Cu Calcd.	%Cu Obs.	%Ni Calcd.	%Ni Obs.	%N Calcd.	%N Obs.	M/512 (cm^{-2} mhos/mole)
$Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	greenish yellow	212d	2.98	13.60	13.54	13.55	13.52	6.29	6.30	5.95	5.90	—
$(dmf)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	green	145	3.02	11.73	11.62	11.55	11.50	5.41	5.43	7.69	7.61	—
$(ua)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	green	203	3.11	12.07	12.01	11.67	11.76	5.09	5.06	10.56	10.50	70.9
$[Ni(Py)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	light green	182d	3.10	9.04	9.06	8.90	8.82	4.17	4.13	9.89	9.86	104.5
$[Ni(anl)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	light green	195d	3.06	8.54	8.50	8.41	8.32	3.94	3.96	9.84	9.89	—
$[Ni(nia)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	yellow	190d	3.15	7.65	7.61	7.53	7.48	3.58	3.51	12.79	12.78	—
$[Ni(pip)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	green	145	3.20	8.85	8.88	8.68	8.67	4.07	4.06	9.06	8.99	—
$[Ni(tol)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	yellow	205	3.18	8.09	8.10	7.96	7.93	3.72	3.67	8.84	8.80	102.4
$[Ni(nap)_4]^{++}[Cu_2(SCN)_2.PPh_3]_2^{--}$	green	212	3.12	7.12	7.06	7.01	6.98	3.24	3.30	7.79	7.74	—
$[Ni(3\text{-}amp)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	brown	205d	3.06	8.40	8.39	8.27	8.25	3.22	3.25	14.38	14.30	—
$[Ni(4\text{-}amp)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	green	178d	3.08	8.40	8.38	8.27	8.32	3.26	3.20	14.38	14.36	111.2
$[Ni(ampn)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	green	225d	3.15	8.47	8.45	8.34	8.35	3.90	3.75	20.37	20.32	—
$[Ni(ben)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	green	215d	3.14	8.58	8.60	8.44	8.41	3.95	3.91	9.49	9.47	—
$[Ni(bipy)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	grey	198	3.18	9.09	9.05	8.95	8.90	4.12	4.03	9.94	9.87	104.5
$[Ni(phen)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	grey	203d	3.20	7.06	7.03	6.95	6.94	3.26	3.23	7.73	7.82	—

d = decomposes.

TABLE 2—ELECTRONIC SPECTRAL BANDS AND SPECTRAL PARAMETERS (cm^{-1})

Complexes	ν_3 $^3A_{2g}\rightarrow{}^3T_{1g}(P)$	ν_2 $^3A_{2g}\rightarrow{}^3T_{1g}(F)$	ν_1 $^3A_{2g}\rightarrow{}^3T_{2g}(F)$	10Dq	B′	β
$Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	25400	15980	9500	10110	750	0.73
$(ua)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	27000	16940	10870	10760	780	0.76
$[Ni(anl)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	26150	16250	10090	10280	785	0.78
$[Ni(nia)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	27000	16660	10870	10480	880	0.80
$[Ni(4\text{-}amp)_4]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	25000	15880	10000	9160	770	0.75
$[Ni(bipy)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	25640	16130	9950	10280	745	0.72

The magnetic susceptibility measurements were carried out by Gouy's method at room temperature using $HgCo(NCS)_4$ as standard. Diamagnetic corrections were made by using Pascals constant.

Results and Discussion

The studies of the complexes have been confined to electronic spectral, magnetic moment, infrared spectral and conductance measurements. Quantitative softness values of the metal ions and of the ligands were also evaluated and used to support the structures proposed on the basis of above studies.

Electronic spectral discussion : To extend support for the stereochemistry around nickel, we have recorded the electronic spectra of some representative complexes and the assignments are given in the Table 2. In all the complexes three bands due to transitions $^3A_{2g}\rightarrow{}^3T_{1g}(P)(\nu_3)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}\rightarrow{}^3T_{2g}(F)(\nu_1)$ are observed. ν_3 is generally observed in the region 25000-27000 cm^{-1}, ν_2 in the region 15000-17000 cm^{-1} and ν_1 in the region 9500-11000 cm^{-1}.

Dq, B′ and β values were calculated using the matrices of Tanabe and Sugano[7] from the values of ν_2 and ν_3.

The position of electronic bands and the values of spectral parameters indicate an octahedral geometry around nickel. This geometry is also supported by magnetic moment values, which are included in Table 1.

Infrared spectral studies :

Lewis acid : $(NCS)_2Ni(NCS)_2Cu_2(Ph_3P)_2$: Analytical data of the compound indicate that two molecules of Ph_3P are coordinated to each molecule of $NiCu_2(SCN)_4$. X-sensitive Wiffens bands of Ph_3P are shifted to higher frequencies which shows that the Ph_3P is coordinated to metal[8,9]. The magnetic moment and electronic spectral data as discussed earlier indicate an octahedral geometry around nickel. On the basis of these results the following structures may be proposed.

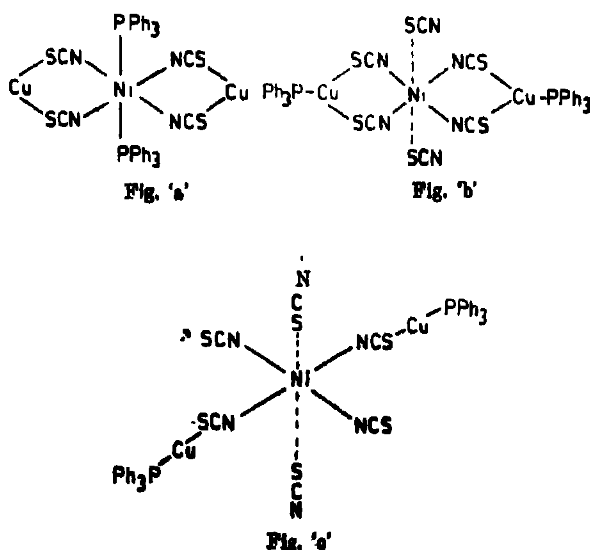


Fig. 'a' Fig. 'b' Fig. 'c'

The structure (c) appears to be more probable due to the following reasons :

(i) The infrared spectral bands due to νCN, νCS and δNCS indicate the presence of only bridged thiocyanate groups[10-13].

(ii) Cu(I) prefers a linear structure instead of angular geometry[8,14]. This also supports structure (c).

(iii) The presence of bands in the region 220-225 cm^{-1} due to νCu-P mode[15] and absence of bands due to νNi-P mode[16] clearly support the structure (c).

(iv) It has been previously observed that whenever Ph_3P is linked to nickel its coordination number does not exceed four and generally planar diamagnetic compounds of nickel are obtained[1,9]. Since our compound is paramagnetic this clearly rules out the linkage of Ph_3P to nickel.

(v) The octahedral geometry is probably achieved by axial linking of S-end of the thiocyanate groups of other layer[17].

Thiocyanate bridged complexes :

$(L)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$; (L = dmf or ua) :

Analytical data show that two molecules of the ligands (dmf or ua) are coordinated to each molecule of $Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$. Triphenylphosphine is coordinated similarly as in Lewis acid as indicated by the infrared spectral band positions. The electronic bands, spectral parameters and magnetic moment values suggest an octahedral environment around nickel. The far ir spectra show the presence of νNi – NCS bands.

On the basis of these results following structures can be postulated. The structure (e) appears to be most probable due to following reasons :

(i) The position of ir spectral bands due to νC – N, νC – S and δNCS modes indicate the presence of both bridged and terminal thiocyanate groups in these sets of complexes[4,8].

(ii) It has been previously observed that whenever nickel is bonded to triphenylphosphine it does not exceed its coordination number beyond four[1,9]. This rules out structure (f).

(iii) Cu(I) prefers linear structure instead of trigonal geometry[8,14] as shown in Fig. e.

(iv) νNi – P bands are generally observed in the region 148-190 cm^{-1} [16] whereas νCu – P stretching bands are assigned in the region 220-230 cm^{-1} [15] by Mores *et al* and in the region 180-230 cm^{-1} by Adams and coworkers[18]. In our complexes we observe bands in the region 220-225 cm^{-1} which could be assigned to νCu – P mode. The bands due to νNi – P mode are absent. This also favours validity of the structure (e).

(v) 'dmf' shows features of coordination through their carbonyl oxygen as is evident by negative shift in νC=O mode[19]. Carbonyl oxygen is donor site in urea also as is evidenced by negative shift in νC=O mode. We observe bands due to νNi – O in the region 370-390 cm^{-1}.

(vi) Octahedral geometry as required by magnetic moment values and electronic spectral studies are also satisfied.

(vii) Linkage of S-end of thiocyanate to Cu(I) and nitrogen (–N) end to Ni(II) are in accordance with HSAB principle[20].

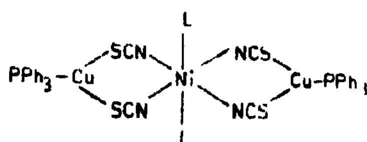


Fig. 'd'

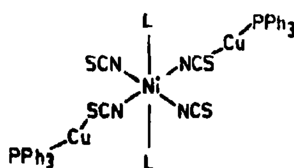


Fig. 'e'

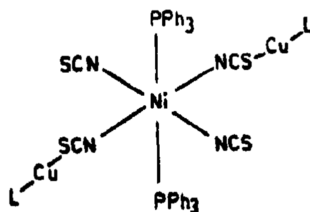


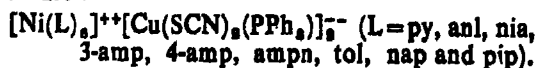
Fig. 'f'

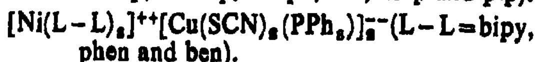
Cationic-Anionic complexes :

$[NiL_n][Cu(SCN)_2(PPh_3)]_2$; (n = 3, when L = bipy, phen and ben, n = 6 when L = py, anl, nia, 3-amp, 4-amp, ampn, tol, nap, pip) : Analytical data indicate that six molecules of py, anl, nia, 3-amp, 4-amp, ampn, tol, nap and pip and three molecules of ben, bipy and phen are coordinated to one molecule of $Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$. The ligands show feature of coordination as is evidenced by positive shifts in the bands of ring vibrations[21,22]. Both the ring nitrogen of phen and bipy are involved in coordination. So they act as bidentate ligands. The nitrogen of NH_2 is the donor site in anl, tol, nap and ben as is evidenced by negative shift in νN – H modes[4,23]. The ir spectra show bands due to νC – N, νC – S and δNCS modes in the region 2140-2080 cm^{-1}, 730-780 cm^{-1} and 430-455 cm^{-1} respectively. Bands in these regions are characteristic of S – bonded thiocyanate[4]. The electronic spectral bands, ligand field parameter and magnetic moment values show that the nickel is in octahedral geometry. Complexes formed by py, tol, 4-amp and bipy are soluble in dmf whereas rest are insoluble. Molar conductance of these complexes show

that they are 1 : 1 electrolyte. These complexes have similar magnetic moment values, spectral parameters and electronic bands.

On the basis of the preceding discussion it can be said that these complexes are cationic-anionic as described elsewhere[1,22] and possible cation and anion are :


$[Ni(L)_6]^{++}[Cu(SCN)_2(PPh_3)]_2^{--}$ (L = py, anl, nia, 3-amp, 4-amp, ampn, tol, nap and pip).


$[Ni(L-L)_3]^{++}[Cu(SCN)_2(PPh_3)]_2^{--}$ (L – L = bipy, phen and ben).

The following points also support the proposed structures :

(i) The linkage of – S end of thiocyanate to Cu(I) is in accordance with HSAB principle.

(ii) Presence of bands in the region 270-290 cm^{-1} can be assigned to νNi – L mode[23,24].

(iii) νCu – P bands are present in all the complexes.

(iv) The $\Delta TE_n^{\dagger}$ (Ni – Cu) values as discussed later also support the proposed structure.

(v) Octahedral coordination around nickel as required by electronic spectral and magnetic moment values are also satisfied.

Quantitative softness values and structure of the complexes :

The proposed structures of complexes can also be supported by quantitative values of softness. The ligands on reaction with $Ni(NCS)_2Cu_2(SCN)_2(PPH_3)_2$ have the choice of coordination either to Ni(II) or to Cu(I) as shown in Figs. x and y respectively.

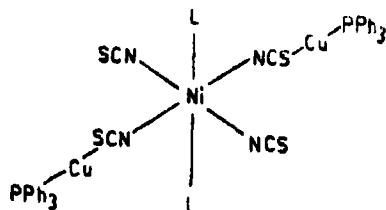


Fig. 'x'

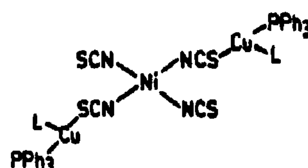


Fig. 'y'

In the preceding discussion structure (x) h[as] been preferred. This is supported by calculating tot[al] softness difference values of nickel and copper[25] b[y] adopting following equations :

$$TE_n^{\dagger}(Ni) = E_n^{\dagger}(Ni) + 2E_m^{\dagger}(L) + 4E_m^{\dagger}(NCS)$$

$$TE_n^{\dagger}(Cu) = 2E_n^{\dagger}(Cu) + 2E_m^{\dagger}(SCN) + 2E_m^{\dagger}(PPh_3)$$

$$\Delta TE_n^{\dagger}(Ni-Cu) = TE_n^{\dagger}(Ni) - TE_n^{\dagger}(Cu) \quad \ldots (\text{[1])}$$

$TE_n^{\dagger}(Ni)$ and $TE_n^{\dagger}(Cu)$ are the total softness [of] the nickel and copper in complexes, respectivel[y]. $E_m^{\dagger}(-NCS)$ and $E_m^{\dagger}(SCN)$ are the softness of – N en[d] and – S end of thiocyanates attached to nickel an[d] copper respectively.

$$TE_n^{\dagger}(Ni) = E_n^{\dagger}(Ni) + 4E_m^{\dagger}(NCS)$$

$$TE_n^{\dagger}(Cu) = 2E_n^{\dagger}(Cu) + 2E_m^{\dagger}(L) + E_m^{\dagger}(SCN) + 2E_m^{\dagger}(PPh_3)$$

$$\Delta TE_n^{\dagger}(Ni-Cu) = TE_n^{\dagger}(Ni) - TE_n^{\dagger}(Cu) \quad \ldots (\text{[2])}$$

Similarly the total softness difference values f[or] structure (y) has been calculated by usin[g] equation (2).

The structure, in which total softness differenc[e] value is higher, will be the most probable[26]. Th[e] $\Delta TE_n^{\dagger}$(Ni – Cu) values are higher for structure (x[)] which shows that our proposed structure is correct.

TABLE 3—IR SPECTRAL BAND POSITIONS (cm^{-1})

Complexes	νC – N	νC – S	δNCS	νNi – L	νNi – NCS	νCu – P
$Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	2160s, 2095s	745s, 740s	450s	—	250w	220w
$(dmf)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	2160sh, 2095s	745s	450w	390m	240w	225w
$(ua)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	2160m, 2120vs	745s, 775m	470w	370w	240m	228w
$[Ni(py)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2120s, 2095s	752sh, 740s	480br	280sh	—	225m
$[Ni(anl)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2115vs, 2080s	755s, 740s	430w	278sh	—	222w
$[Ni(nia)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2140w, 2085s	780w, 740s	480w	280w	—	220w
$[Ni(pip)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2180s, 2090sh	750m	450w	290sh	—	220w
$[Ni(tol)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2120s, 2095s	750sh, 740s	450w	290w	—	220w
$[Ni(nap)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2120s, 2085s	760m, 740s	425br	290w	—	225w
$[Ni(3\text{-}amp)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2130sh, 2095vs	785w, 745s	435w	278sh	—	225m
$[Ni(4\text{-}amp)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2120sh, 2100vs	740s	485m	280w	—	220w
$[Ni(ampn)_6]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2140s, 2095s	745s, 780s	455s, 430m	280sh	—	220m
$[Ni(ben)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2115vs, 2092s	740s, 785s	435w	292w	—	225w
$[Ni(bipy)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2115sh, 2095s	760s, 740s	440w	275w	—	225w
$[Ni(phen)_3]^{++}[Cu(SCN)_2.PPh_3]_2^{--}$	2100s, 2090s	785w, 740s	480w	280m	—	225m

s = strong, vs = very strong, w = weak, m = medium, br = broad and sh = shoulder.

TABLE 4—SOFTNESS OF LIGANDS AND TOTAL SOFTNESS DIFFERENCE

Complexes	$E_m^{\ddagger}$ (ligand)	$\Delta TE_n^{\ddagger}$ (Ni−Cu) (structure x)	$\Delta TE_n^{\ddagger}$ (Ni−Cu) (structure y)
$(dmf)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	−10.65	54.12	22.17
$(ua)_2Ni(NCS)_2Cu_2(SCN)_2(PPh_3)_2$	−10.42	53.38	22.40
$[Ni(py)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.75	17.68	8.92
$[Ni(anl)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.54	16.42	7.66
$[Ni(nia)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−13.90	30.58	21.82
$[Ni(pip)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.39	15.52	6.76
$[Ni(tol)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.38	15.46	6.70
$[Ni(nap)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.41	15.64	6.88
$[Ni(amp)_4]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−12.02	19.30	10.54
$[Ni(ampn)_2]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.27	14.80	6.04
$[Ni(bipy)_2]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.70	17.38	8.62
$[Ni(phen)_2]^{++}[Cu(SCN)_2.PPh_3]_2^-$	−11.98	19.06	10.30

(i) The $E_m^{\ddagger}$ values of N(−NCS), S(−SCN) and PPh_3 have been taken as −12.65, −8.82 and −7.78 respectively.

(ii) The $E_n^{\ddagger}$ values of Ni(II) and Cu(I) have been taken as −0.82 and −2.65 respectively.

The $\Delta TE_n^{\ddagger}$(Ni − Cu) values are also calculated for ationic-anionic complexes. These data as indicated n Table 4 show that PPh_3 is coordinated to ;u(I) and other ligands of the present series to Ni(II).

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eferences

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Complexes of *p-p'-bis*(benzoyl thiourea)Benzene with Cu(II), Ni(II) and Co(II) Salts and Their Biological Activity

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Metal complexes of the type, [M(BBTuB)X_2] [where M=Cu(II), Ni(II), Co(II); BBTuB=*p-p'-bis*(benzoyl thiourea)benzene and X=Cl^-, Br^-, NO_3^-, ClO_4^-] have been prepared and characterized on the basis of ir spectra, electronic spectra and magnetic susceptibility measurements. Infrared spectra manifest the coordination of the ligand to the metal ion through carbonyl oxygen and thiocarbonyl sulphur atoms. The complexes possess octahedral stereochemistry as inferred from electronic spectral data and magnetic moment values. Fungicidal screening of the complexes shows them to be antifungal against *A. niger*, *F. oxysporum* and *H. oryzae*.

As a part of our investigations on the synthesis and structure elucidation of metal complexes of sulphur donor ligands[1-7], we report in the present communication the preparation and characterization of some metal complexes with *p-p'-bis*(benzoyl thiourea) benzene along with their fungicidal activity.

Experimental

The ligand, *p-p'-bis*(benzoyl thiourea)benzene was synthesized by reacting *p*-phenylene diamine, benzoyl chloride and ammonium thiocyanate in acetone medium[8]. It was recrystallized from DMF-alcohol mixture.

A DMF solution of the ligand was treated with an alcoholic solution of the appropriate metal(II) salt in the molar ratio 1 : 1 and the mixture was refluxed for 3-4 hr. The refluxed solution was reduced in volume and cooled when solids separated out which were filtered, washed with DMF-alcohol mixture and analysed after drying in vacuum.

The complexes are highly insoluble in water but sparingly soluble in dioxane and DMF. All the complexes decompose above 250°. Metal, sulphur and nitrogen content of the complexes were determined by Vogel's methods[9]. The analytical data are recorded in Table 1.

IR spectra of the ligand and the complexes were recorded on a Perkin Elmer model 221 Spectrophotometer in KBr pellets. Magnetic susceptibilities were measured by Gouy method using Mercury(II) tetrathiocyanato cobaltate(II) as the standard. Dimagnetic corrections were made using standard values[10]. Electronic spectra of the ligand and the metal complexes were recorded in dioxane.

Results and Discussion

The infrared spectrum of the ligand shows a strong and broad band in the region 3240-2990 cm^{-1} corresponding to ν_{NH} vibrations being overlapped with the ν_{CH} vibrations of the phenyl group. This band remains almost unaffected in the metal complexes indicating the non-involvement of NH group in bond formation. Another strong band appears at ~1660 cm^{-1} in the ligand and may be assigned to $\nu_{C=O}$ vibrations. This undergoes a shift to lower frequency region in the metal complexes and appears at ~1640 cm^{-1}. The shift suggests the *coordination of carbonyl group to the metal ion.*

A strong and broad band is observed in the frequency region 1600-1400 cm^{-1} of the ligand as well as in the metal complexes which most probably arises due to phenyl ring vibrations. Phenyl groups usually show four vibrational bands in this region which are of weak to medium in intensity. Another band of considerable intensity appears at 1150 cm^{-1}. We assign this band to ν_{C-N} vibrations. Besides, a medium band is also observed at 705 cm^{-1} which is susceptible to coordination and arises due to $\nu_{C=S}$ vibrations. As reported earlier[11] coordination of metal through sulphur leads to a decrease in $\nu_{C=S}$ frequency and an increase in ν_{C-N} frequency. In the metal complexes the C–N band undergoes a positive shift and appears at ~1170 cm^{-1}. On the other hand the C=S band lowers by 25-30 cm^{-1} in the metal complexes which clearly implies the coordination of sulphur atom to the metal ion.

There are two to three bands observed in the spectra of the ligand in the region 700-650 cm^{-1}. These bands shift in an irregular way in the metal complexes.

Coordination of NO_3^- group[12] to the metal ion is evident by the presence of a medium band near about 1010 cm^{-1}. In the perchlorato complex we get three additional bands at ~1250(w), 1140(s) and 990(w) cm^{-1} which can be attributed to ν_8, ν_6 and ν_1 vibrations[13] respectively.

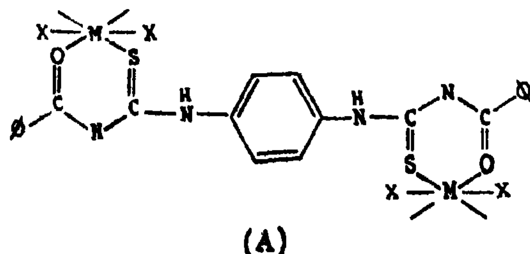
All the complexes are paramagnetic (Table 1). Electronic spectra of Cu(II) complexes show a

TABLE 1—ANALYTICAL DATA OF *p,p'-bis*(BENZOYL THIOUREA)BENZENE (BBTuB) AND ITS METAL COMPLEXES

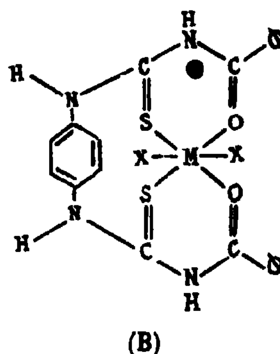
Compound	Colour	μ_{eff} in B.M. (29°±1°C)	Found(Calcd.)% Metal	Sulphur	Nitrogen
BBTuB	Grey			14.65 (14.72)	12.55 (12.90)
[Cu(BBTuB)Cl$_2$]	Dirty green	1.72	10.88 (11.17)	11.02 (11.25)	9.78 (9.85)
[Cu(BBTuB)Br$_2$]	Leaf green	1.715	9.62 (9.66)	9.65 (9.78)	8.39 (8.51)
[Cu(BBTuB)(NO$_3$)$_2$]	Brown	1.72	10.12 (10.22)	10.01 (10.29)	9.00 (9.01)
[Cu(BBTuB)(ClO$_4$)$_2$]	Light green	1.72	8.94 (9.12)	9.00 (9.18)	7.98 (8.04)
[Co(BBTuB)Cl$_2$]	Grey	4.61	10.08 (10.46)	11.09 (11.34)	9.39 (9.57)
[Co(BBTuB)Br$_2$]	Grey	4.58	8.81 (9.02)	9.65 (9.80)	8.36 (8.57)
[Co(BBTuB)(NO$_3$)$_2$]	Green	4.62	8.45 (9.55)	10.26 (10.37)	8.79 (9.07)
[Co(BBTuB)(ClO$_4$)$_2$]	A. O. grey	4.55	8.02 (8.51)	9.11 (9.27)	7.90 (8.09)
[Ni(BBTuB)Cl$_2$]	New olive green	2.80	9.86 (10.41)	11.02 (11.35)	9.12 (9.57)
[Ni(BBTuB)Br$_2$]	New s. o. grey	2.64	8.52 (8.99)	9.51 (9.80)	8.09 (8.57)
[Ni(BBTuB)(NO$_3$)$_2$]	Pale rose	2.62	8.91 (9.52)	10.28 (10.38)	8.87 (9.07)
[Ni(BBTuB)(ClO$_4$)$_2$]	Light green	2.615	8.28 (8.48)	9.12 (9.24)	7.88 (8.09)

broad assymetric ligand field band in the region 13,000-17,000 cm^{-1} whose maxima lie at 15000 cm^{-1} corresponding to $^2E_g \longrightarrow ^2T_{2g}$ transition in a nearly octahedral arrangement. A charge-transfer band also appears at ~27,000 cm^{-1}. Co(II) complexes show an intense band in the region 16,000-17,000 cm^{-1} which can be assigned to $^4T_{1g}(F) \longrightarrow ^4T_{1g}(P)$ transition in an approximately octahedral field. Ni(II) complexes resolve three bands at about 11,000, 14,000 and 27,000 cm^{-1}. In an octahedral approximation these bands can be assigned to $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ transitions respectively. Co(II) and Ni(II) complexes possess low magnetic moments. The lower values may be attributed to antiferromagnetic interaction.

Based on the foregoing spectral features and magnetic moment values one of the probable structures (A or B) may be suggested for the complexes. The complexes are highly insoluble in water and common organic solvents. This seems to suggest a polymeric nature for the complexes (A) wherein each ligand molecule coordinates towards two metal ions in *trans* bi-bidentate form involving sulphur and oxygen atoms.



(A)



(B)

Fungicidal activity : The antifungal activity of the ligand and its metal complexes was assayed by the method of Horsfall[14] using the agar plate technique. The percentage of inhibition was

TABLE 2—FUNGICIDAL SCREENING
AVERAGE PERCENTAGE INHIBITION AFTER 5 DAYS OF COLONY GROWTH AT 100 ppm., TEMP.=31°±1°C

Sl. No.	Compound	Organism *A. niger*	*F. oxysporum*	*H. oryzae*
1.	BBTuB	51.5	53.8	38.6
2.	[Cu(BBTuB)Cl$_2$]	92.5	76.9	55.2
3.	[Cu(BBTuB)Br$_2$]	55.9	59.5	65.4
4.	[Cu(BBTuB)(NO$_3$)$_2$]	57.4	55.0	68.3
5.	[Cu(BBTuB)(ClO$_4$)$_2$]	52.3	62.9	58.6
6.	[Co(BBTuB)Cl$_2$]	88.2	58.3	91.8
7.	[Co(BBTuB)Br$_2$]	72.5	56.9	79.8
8.	[Co(BBTuB)(NO$_3$)$_2$]	28.6	42.9	25.7
9.	[Co(BBTuB)(ClO$_4$)$_2$]	25.9	33.8	29.5
10.	[Ni(BBTuB)Cl$_2$]	56.4	57.0	51.9
11.	[Ni(BBTuB)Br$_2$]	55.6	59.8	58.3
12.	[Ni(BBTuB)(NO$_3$)$_2$]	89.8	58.0	65.4
13.	[Ni(BBTuB)(ClO$_4$)$_2$]	75.2	65.6	78.5

calculated as reported earlier[7]. The fungicidal activity of various compounds is summarised in Table 2. The data reveal that all the complexes except compound nos. 8 and 9 are physiologically more active than the ligand. The reason may perhaps be due to the presence of C=O and C=S groups in the ligand as well as its complexes. This observation is more or less in accordance with the observation of Horsfall and coworkers[15]. Hence all the compounds except nos. 8 and 9 may serve as antifungal agents against the organisms studied.

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Protonation Constants and Thermodynamic Parameters of 3-Bromo-2-Hydroxy-5-Methylacetophenone, Its Oxime and *n*-Propylimine

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Potentiometric studies have been carried out on 3-bromo-2-hydroxy-5-methylacetophenone, its oxime and *n*-propylimine in dioxane-water (20 to 75%, v/v) media at different ionic strengths 0.02*M*, 0.05*M* and 0.1*M* ($NaClO_4$) and temperatures 25, 30 and 35°. The thermodynamic parameters viz. ΔG, ΔH and ΔS were evaluated.

THE complexing properties of *o*-hydroxyacetophenone and their Schiff bases derived from hydroxylamine and primary amines are of much interest. These ligands have been found to be useful reagents for the estimation of transition metals[1,2]. In the present communication, the protonation constants of 3-bromo-2-hydroxy-5-methylacetophenone (BMHA), 3-bromo-2-hydroxy-5-methylacetophenoneoxime (BMHAO) and 3-brome-2-hydroxy-5-methylacetophenone-*n*-propylimine (BMHA-*n*Pr) have been studied in dioxane-water media at different ionic strengths and temperatures by using Calvin-Bjerrum technique[3].

Experimental

Synthesis of ligands : A 50% acetic acid solution of 2-OH, 5-Me-acetophenone[4] was brominated in ice-bath to form 3-Br, 2-OH, 5-Me-acetophenone (BMHA). The BMHA on condensation[4] with hydroxylamine hydrochloride and *n*-propylamine gave BMHAO and BMHA-*n*Pr.

Materials : The reagents used were all BDH-grade. Pure distilled water was redistilled over alkaline $KMnO_4$. The dioxane was purified[4].

Apparatus : I. T. L. *p*H-meter model M-110 was used for *p*H measurements. The electrode assembly consisted of glass and calomel electrodes dipped in the titration mixture. The *p*H meter was calibrated at *p*H = 4.05 and 9.15 with aqueous potassium hydrogenphthalate and borax buffer respectively.

Potentiometric studies : The following solutions were titrated against standard carbonate free (0.52*M*) sodium hydroxide[5] solution. The total volume was kept 40 ml with 75% v/v dioxane content.

(i) (0.02*M*) $HClO_4$ + (0.08*M*) $NaClO_4$.

(ii) (0.02*M*) $HClO_4$ + (0.08*M*) $NaClO_4$ + (0.004*M*) ligand.

The ionic strengths, $\mu = 0.1M$, 0.05*M* and 0.02*M* were maintained by the addition of appropriate quantities of sodium perchlorate solution. The titrations were carried out in 20-75%(v/v) dioxane-water media maintaining the temperature at 30° ± 1 with the help of a thermostat. The titrations were also carried out at temperatures 25, 30 and 35° and ionic strength $\mu = 0.1M$.

Calculations : The average number of protons ($\bar{n}_A$) associated with ligands was determined from the acid and ligand titration curves employing the equation of Irving and Rossotti[6]. The calculations of protonation constants were carried out by plotting a graph between $\bar{n}_A$ vs *p*H. The log K_1^H values have been obtained at half integral value. The values were also obtained by the equation 1 :

$$\log K_1^H = pH + \log \bar{n}_A/(1 - \bar{n}_A) \quad (1)$$

The values obtained by the two different methods were in good agreement. The average values of log K_1^H are reported in Table 1.

TABLE 1—Log K_1^H VALUES FOR BMHA, BMHAO AND BMHA-*n*Pr AT 30°

Ligands	Dioxane-water%(v/v) $\mu = 0.1M$				Ionic strength(*M*) Dioxane-water(v/v)75%		
	20	40	60	75	0.05	0.02	0.00
BMHA	8.75	9.30	10.05	10.86	11.05	11.18	11.45
BMHAO	8.25	8.82	9.51	10.12	10.22	10.42	10.70
BMHA-*n*Pr	8.51	9.05	9.82	10.36	10.52	10.70	10.96

Discussions

The log K_1^H value (11.85) of *o*-hydroxyacetophenone (HA) was obtained in 75% dioxane-water medium at 30 ± 1° and ionic strength $\mu = 0.1M$ ($NaClO_4$) by Kamat and Dator[7]. In the present case the log K_1^H value for BMHA is 10.86 indicating the enhanced acid strength. The lower value of log K_1^H for BMHA can be ascribed to the strong electron withdrawing nature of the bromine atom situated

at *ortho* position with respect to the phenolic $-OH$. The electron releasing effect of the methyl group present at position-5, though should reduce the acid strength of BMHA, is not much significant due to enlarged distance over which it has to operate. The intramolecular hydrogen bonding between hydrogen of phenolic $-OH$ and oxygen of $\rangle C=O$ group which may lower the acid strength of BMHA, is also not very effective. The $-I$ effect exerted by bromine dominates.

It is interesting to note the effect of the presence of the azomethin group ($\rangle C=N-$) in place of the keto group. The keto-oxime (BMHAO) and the keto-imine (BMHA-*n*Pr) are found to be more acidic than the ketone (BMHA) as is evident by their lower log K_1^H values 10.16 and 10.36 respectively. This may be due to the presence of O–H... N bond which is weaker than O–H.. O bond present in the ketone BMHA. The release of phenolic hydrogen in keto-oxime and keto-imine will be promoted. Further it has also been observed that the keto-oxime (BMHAO) is more acidic than the keto-imine (BMHA-*n*Pr). This may be due to the possibility of hydrogen bond formation by oxygen of phenolic group and hydrogen of oximino group which imparts additional stability to anion derived from the oxime (BMHAO)

Effect of dioxane content : The dielectric constant of the medium decreases with increase in dioxane percentage[9]. It has been observed that log K_1^H values for all the compounds under consideration increase with increase in dioxane percentage indicating the fall in acid strength of the compounds. The electrostatic force between the ions increases with decrease in dielectric constant thus facilitating the formation of molecular species by suppressing the ionization, resulting in an increase in log K_1^H values[9]. The variation of log K_1^H values with dioxane percentage is depicted in Fig. 1.

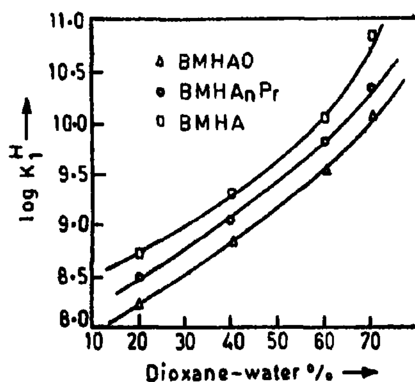


Fig. 1

Effect of ionic strength: No change in the shape of formation curves drawn at different ionic strengths was observed. This suggests that the various species co-exist in the solution. The interaction of ions decreases with increase in μ-values of the medium as log K_1^H values are found to decrease. From the graph between log K_1^H vs $\sqrt{\mu}$, as depicted in Fig. 2, the protonation constants at zero ionic strength were obtained by extrapolation of the values of log K_1^H to zero ionic strength. The values are reported in Table 1.

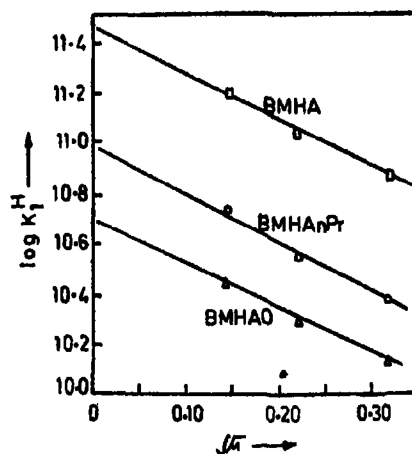


Fig. 2

Effect of temperature : The log K_1^H values at temperatures 25, 30 and 35° have been recorded in Table 2. The thermodynamic parameters viz. ΔG, ΔH and ΔS have been calculated from equations 2,3 and 4 respectively. The values are recorded in Table 2.

$$\Delta G = -2.303\, RT \log K \qquad .. \quad (2)$$

$$\Delta H = 2.303R \frac{T_2 \times T_1}{T_2 - T_1} \log \frac{K''}{K'} \qquad ... \quad (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad ... \quad (4)$$

It is concluded that with the change in temperature there was no appreciable change in the values of protonation constants and thus temperature has no significant effect on the acid strengths of these ligands. The negative values of ΔH indicate that the protonations of the ligands are accompanied by liberation of heat and the process is exothermic[10]. The high positive values of ΔS indicate that the protonations of the ligands tend to proceed spontaneously[11].

TABLE 2—PROTONATION CONSTANTS AND THERMODYNAMIC PARAMETERS FOR BMHA, BMHAO AND BMHA-*n*Pr AT μ=0.1*M*($NaClO_4$) IN 75%(v/v) DIOXANE-WATER MEDIUM

Ligands	Temperature °C	log K_1^H	$-\Delta G$ K. cal./mole	$-\Delta H$ K. cal./mole	ΔS cal./deg./mole
BMHA	25	10.92	15.10		
	30	10.86	14.98	5.06	32.8
	35	10.80	14.90		
BMHAO	25	10.17	14.21		
	30	10.12	14.04	4.04	32.6
	35	10.08	13.82		
BMHA-*n*Pr	25	10.42	14.59		
	30	10.36	14.36	4.46	32.7
	35	10.32	14.22		

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Differential Refractometric and Conductometric Studies on the Charge-Transfer Interaction of Some Metal β-Diketonates with Iodine*

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In order to provide further evidence on the site of interaction in metal β-diketonate chelate rings, the charge-transfer interaction of $M(acac)_n$ [M=Be(II), Al(III), Fe(III), Cr(III), Co(III), VO(IV), Zr(IV), Th(IV)], $M(BA)_n$ [M=Cu(II), Al(III), Cr(III), Co(III)] and $M(DBM)_n$ [M=Cu(II), Pd(II), Al(III)] with iodine have been studied in solvents of different dielectric permittivity using differential refractometric and conductometric measurements. The K_1, α, σ and ρ in these solvents have been calculated and the role of dielectric permittivity of the solvents in the complex formation and its limitations for these techniques have been explored and discussed. These data support interaction from the π-electron pool of the pseudo-benzenoid chelate rings of metal β-diketonates.

SPECTROPHOTOMETRIC[1], dielectric[2,3] and refractometric[4,5] studies have indicated that some metal acetylacetonates form molecular complexes with iodine by donation of electron density from the chelate rings to σ^*-orbital of iodine. But the high equilibrium constant (K_1) obtained in these cases in comparison to benzene-iodine system may create a doubt whether the donation takes place from π-electron pool of the chelate rings or n-electrons of oxygen atom of the chelate. In our dielectric[2,3] and refractometric[4,5] studies, solute-solvent interaction was observed and the nature of this interaction was noted to be almost the same as was found for benzene-solvent interaction. On the one hand these data strengthen the $\pi \rightarrow \sigma^*$ transition, but on the other hydrogen bonding of $Th(acac)_4$ with nitrophenols through oxygen atom favours $n \rightarrow \sigma^*$ transition[6]. In order to provide further evidence on the site of interaction in these chelate rings, the charge-transfer interaction of some metal acetylacetonates, $M(acac)_n$ [where M = Be(II), Al(III), Fe(III), Cr(III), Co(III), VO(IV), Zr(IV), Th(IV)], metal benzoylacetonates, $M(BA)_n$ [where M=Cu(II), Al(III), Cr(III), Co(III)] and metal dibenzoyl methanates, $M(DBM)_n$ [where M= Cu(II), Pd(II), Al(III)] with iodine (acceptor) have been studied using differential refractometric and conductometric measurements and the role of dielectric permittivity of the solvents in these interactions and its limitations for these techniques have been explored and discussed.

Experimental and data analysis

The materials used and method of experimentation were essentially the same as reported earlier[4,5]. The electrical conductance of donors, acceptor and donor-acceptor complexes have been measured by Philips – PR9500 conductivity bridge and a conductivity cell having cell constant 0.982. All measurements were carried out at 50 cycles per second at 30°. Before measuring the electrical conductance, the cell constant was calibrated each day by 0.1*N* KCl solution. The refractive index of solutions were measured with the help of Bausch and Lomb refractometer with an accuracy of ±0.0002 at 30°. The conductivity experiments have been performed in two ways :

(i) In order to use equation(1) to evaluate K_1 of these complexes, the concentration of acceptor was kept constant and the concentration of donors was varied.

(ii) By using Gutmann's method[7] to study the charge-transfer interaction, the equimolar stock solutions of donors and acceptor in appropriate solvents were mixed keeping the total volume constant and varying the volume of donor and acceptors.

The equilibrium constant (K_1) by electrical conductance method[8] was measured in each case employing equation (1).

$$\delta\Lambda/C_D^{\circ} = \{K_1 C_A^{\circ}/\rho(1+K_1 C_A^{\circ})\} - \{K_1 \delta\Lambda/(1+K_1 C_A^{\circ})^2\} \quad \ldots (1)$$

where C_A° and C_D° are the initial concentrations of acceptor and donor, respectively and ρ is the extent of polarization. $\delta\Lambda$ is the difference in electrical conductance of solution (donor+acceptor) and solvent. A plot of $\delta\Lambda$ vs $\delta\Lambda/C_D^{\circ}$ was linear with a

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ope $= -K_1/(1+K_1C_A^0)^2$ and intercept $=K_1C_A^0/\rho$ $(1+K_1C_D^0)$. Conductometric titration technique as indicated 1 : 1 stoichiometry of these complexes.

The equilibrium constant (K_1) and extent of electronic polarization (α) from differential refractometric method have been calculated by using equation (2) recently developed by Sahai *et al*[9].

$$\Delta\Omega C_{DA}/C_D^0 = \{K_1C_A^0/\alpha(1+K_1C_A^0)\} - \{K_1\Delta\Omega C_{DA}/(1+K_1C_A^0)^2\} \quad \dots (2)$$

here the notations have their usual meanings and their values have been calculated as reported earlier[9]. As expected from equation (2), a plot of $\Delta\Omega C_{DA}$ vs $\Delta\Omega C_{DA}/C_D^0$ was linear (Fig. 1) with a slope $= -K_1/(1+K_1C_A^0)^2$ and intercept $=K_1C_A^0/\alpha$ $(1+K_1C_A^0)$. Differential refractometric titration technique has also indicated 1 : 1 stoichiometry of these complexes.

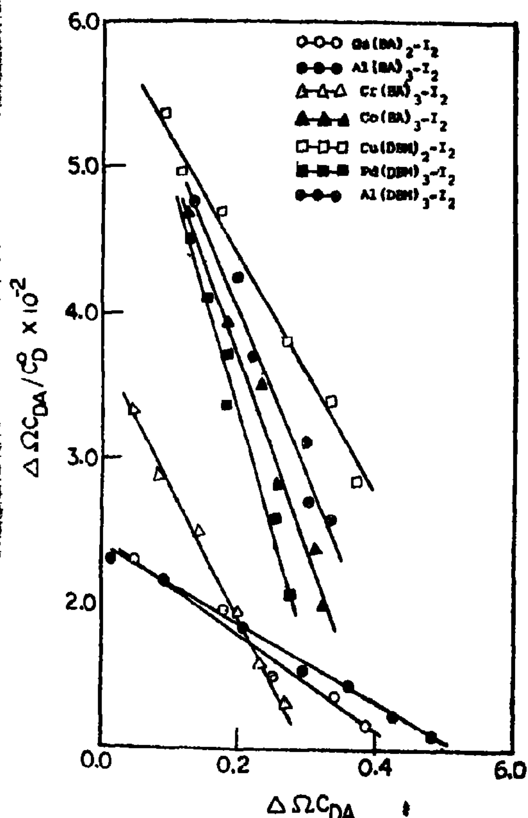


Fig. 1. Plots of $\Delta\Omega C_{DA}$ vs $\Delta\Omega C_{DA}/C_D^0$ for molecular complexes of some metal β-diketonates with iodine in CCl_4 at 30°.

The K_1 has also been calculated using Yoshida and Osawa's[10] equation (3),

$$K_1 = 2\sqrt{k}\{\sqrt{k}(C+C') - (C+kC')\}/(C-kC')^2 \quad \dots (3)$$

where C and C' are the maximum concentration of both the systems and k is the maximum deviation from the additive line when molar ratio of solutes is plotted against square of refractive index (n^2). The K_1 has also been calculated by modified Yoshida and Osawa's method as developed by Sahai and Singh[11]. In this method, instead a plot of n^2 vs molar ratio of solutes, $\Delta\Omega C_{DA}$ is plotted against molar ratio of solutes which have indicated 1 : 1 stoichiometry of these complexes. The stoichiometry of these complexes has also been calculated by plotting $\phi_D C_A^0$ (or $\phi_D/\Delta\phi_{DA}C_A^0$) against X_D (mole fraction of donor), the maxima occur at $X_D=n/(1+n)$. At this maxima if $n=1$, then K_1 may be calculated by equation (4) as recently developed by Sahai *et al*[12].

$$K_1 = (\phi_D/\Delta\phi_{DA})/(C_D^0)(1-\phi_D/\Delta\phi_{DA})^2 \quad (4)$$

where $\Delta\phi_{DA}=\phi_{DA}-\phi_{CD}$ and $\phi_{CD}=\phi-\phi_D$. These values have been calculated as reported earlier[12,13].

Results and Discussion

The equilibrium constants (K_1) of the charge-transfer complexes of metal β-diketonates with iodine have been calculated by observing the refractive indices of solvent, acceptor, donor and solution (donor+acceptor). The refraction per cm^3 of solvent (ϕ_0), acceptor (ϕ_A), donor (ϕ_D) and solution (ϕ) were then calculated as reported earlier[4,8,11-13]. From these data, the difference in refraction per cm^3 of solution and solvent ($\delta\phi$), solution and acceptor ($\Delta\phi_A$), solution and donor ($\Delta\phi_D$) and the refraction per cm^3 due to charge-transfer complex ($\Delta\Omega C_{DA}$) have been calculated. An appreciable increase in $\delta\phi$, $\Delta\phi_A$, $\Delta\phi_D$ and $\Delta\Omega C_{DA}$ values with the increase of donor concentration and keeping the acceptor concentration constant have been interpreted due to the charge-transfer from the π-orbital of pseudo-benzenoid ring of metal β-diketonates to the σ*-orbital of iodine. This is in parallel agreement with our earlier observations[1,4]. The best values of equilibrium constant and related parameters have been obtained when differential refractometric method has been applied. The K_1 calculated from this method applying several techniques (equations 2, 3 and 4) are recorded in Table 1. These values are quite comparable with those obtained from spectrophotometric method[1].

Gutmann *et al*[14,15] have shown that the appearance of a peak in conductivity concentration (of D and A) plot is a clear indication of complex formation between donor(D) and acceptor(A). Since the conductivities (σ) are additive, it follows that σ in the absence of interaction should be linearly related to the concentration of the titrant. The stoichiometry of the complex may be deduced from the concentrations of D and A at the conductivity peak. A representative plot is shown in Fig 2. The value of the conductivity peak above a base line connecting the conductivities of pure donor and acceptor solution is a measure of the excess conductivity caused by the formation and subsequent dissociation of the complex. The

TABLE 1 – COMPARISON OF DIFFERENTIAL CONDUCTOMETRIC AND REFRACTOMETRIC EQUILIBRIUM CONSTANT AND RELATED DATA* FOR 1 : 1 MOLECULAR COMPLEXES OF METAL β-DIKETONATES WITH IODINE AT 30° IN : 1. CCl_4(ϵ=1.96); 2. CCl_4+CH_3CN(3 : 1 ; ϵ=10.89); 3. CCl_4+CH_3CN(1 : 1 ; ϵ=19.60); 4. CCl_4+CH_3CN(1 : 3 ; ϵ=28.78); 5. CH_3CN(ϵ=37.50)

System/ Solvent	Conductometric data			Refractometric data				
	K_1 (l. mol^{-1}) Eq. 1	$\sigma_g \times 10^6$	ρ	K, (l. mol^{-1}) Eq. 2	K, (l. mol^{-1}) Eq. 3	K, (l. mol^{-1}) Eq. 4	$\alpha \times 10^6$	$\Delta\Omega G$ maxi
1	2	3	4	5	6	7	8	9
$Be(acac)_2$-I_2								
1.	10.82	8.0	100.00	20.00	20.72	19.28	12.41	0.6
2.	12.80	19.0	120.00	16.00	17.25	17.46	11.20	0.5
3.	13.40	45.0	140.45	14.00	14.55	15.12	11.19	0.5
4.	14.20	58.0	165.55	12.04	12.20	13.24	11.02	0.5
5.	15.70	72.0	200.00	10.62	11.46	10.46	10.86	0.4
$Al(acac)_3$-I_2								
1.	110.45	8.2	160.28	174.41	179.20	183.00	0.75	0.4
2.	130.28	40.0	171.55	165.55	172.46	180.00	0.62	0.41
3.	140.40	120.0	180.00	145.40	162.56	172.46	0.56	0.4
4.	151.46	220.0	185.42	185.40	145.22	158.55	0.52	0.38
5.	160.00	380.0	200.00	120.30	140.45	150.45	0.51	0.36
$Fe(acac)_3$-I_2								
1.	640.55	—	200.45	256.41	245.79	269.18	1.04	0.48
2.	710.28	—	210.10	250.00	240.35	250.14	1.00	0.46
3.	740.56	—	230.35	245.00	231.25	235.45	0.95	0.45
4.	800.00	—	250.45	232.20	220.35	210.20	0.80	0.42
5.	820.34	—	260.52	220.00	210.85	186.26	0.70	0.40
$Cr(acac)_3$-I_2								
1.	880.45	12.2	340.25	833.33	842.87	892.85	1.68	0.66
2.	910.28	80.0	360.65	820.00	810.46	865.46	1.60	0.60
3.	940.45	210.0	390.45	800.00	742.45	810.52	1.58	0.58
4.	960.00	340.0	400.00	740.45	720.56	800.46	1.40	0.57
5.	1000.00	415.0	450.50	720.20	700.46	780.85	1.35	0.54
$VO(acac)_2$-I_2								
1.	1410.46	13.8	400.00	952.38	918.26	897.42	2.31	0.69
2.	1460.85	130.0	410.00	920.00	900.02	860.28	2.30	0.67
3.	1520.28	250.0	420.40	905.00	850.46	810.45	2.20	0.62
4.	1580.45	350.0	430.45	840.00	810.23	780.32	2.10	0.60
5.	1620.00	440.0	485.45	780.45	760.10	710.46	2.00	0.58
$Co(acac)_3$-I_2								
1.	1420.35	14.2	310.45	1176.47	1068.47	1088.88	2.76	0.72
2.	1480.75	140.0	330.20	1120.45	1020.20	1030.35	2.70	0.70
3.	1510.50	265.0	340.45	1100.00	1000.00	960.56	2.43	0.68
4.	1570.20	365.0	400.00	1040.45	960.65	910.35	2.35	0.67
5.	1610.35	480.0	420.45	1000.00	920.45	840.56	2.20	0.65
$Zr(acac)_4$-I_2								
1.	1440.35	15.5	375.60	1175.00	1175.91	1185.84	2.90	0.74
2.	1520.46	180.0	385.55	1110.45	1140.56	1110.45	2.68	0.71
3.	1560.28	370.0	400.00	1040.30	1060.28	1080.40	2.10	0.70
4.	1580.46	480.0	410.24	1000.20	1000.00	1020.56	2.10	0.68
5.	1610.00	520.0	420.35	940.45	940.20	980.32	2.00	0.65
$Th(acac)_4$-I_2								
1.	2010.30	16.2	365.75	2120.00	2118.12	2172.49	3.25	0.91
2.	2115.28	185.0	370.75	2080.56	2100.00	2120.56	3.00	0.90
3.	2210.55	390.0	380.35	2040.40	2040.46	2100.00	2.85	0.86
4.	2240.45	510.0	400.00	2000.00	2000.00	2040.56	2.75	0.82
5.	2300.00	545.0	410.35	1940.45	1940.50	2000.00	2.60	0.80
$Cu(BA)_2$-I_2								
1.	200.00	9.8	275.00	320.00	335.00	345.00	1.06	0.52
2.	210.85	57.8	280.00	300.20	320.00	320.00	1.00	0.50
3.	230.40	155.0	300.45	270.45	310.46	300.45	0.80	0.48
4.	240.46	281.4	310.45	250.60	286.40	250.46	0.75	0.46
5.	265.55	373.0	320.45	230.20	260.35	240.35	0.70	0.42

(*Table 1 Contd.*)

1	2	3	4	5	6	7	8	9
$Al(BA)_3$-I_2								
1.	160.55	9.2	260.00	270.00	278.00	282.00	1.00	0.51
2.	200.25	40.0	265.42	250.55	255.23	260.46	0.90	0.50
3.	210.46	130.0	280.80	240.35	230.46	230.46	0.80	0.48
4.	240.46	270.0	290.95	220.35	220.35	200.40	0.70	0.46
5.	260.35	365.0	300.00	200.00	200.20	180.56	0.60	0.45
$Cr(BA)_3$-I_2								
1.	850.50	14 0	240.00	906.00	925.00	930.00	2.20	0.66
2.	900 85	145 0	245.00	900.00	900.25	910.46	1.98	0.65
3.	940.35	282.0	250.56	840.46	860.35	880.46	1.90	0.62
4.	1000.00	402.0	260.00	810.30	800.46	810.85	1.80	0.60
5.	1020.35	475.0	365.55	800.45	760.35	800.35	1.72	0.57
$Co(BA)_2$-I_2								
1.	1000.00	17 0	330.80	1240.00	1265.00	1180.75	3.00	0.78
2.	1040.40	142.0	340.40	1210.45	1220.46	1120.75	2.80	0.76
3.	1100.00	284.0	345.50	1180.55	1140.56	1080.56	2.65	0.72
4.	1140.45	420.0	360.80	1120 45	1090.30	1060.40	2.40	0.70
5.	1200 00	475.0	380 80	1040.60	1020.20	1000.20	2.00	0.66
$Cu(DBM)_2$-I_2								
1.	1260.45	14.5	330.50	1505.04	1520.00	1430.00	3.20	0.82
2.	1300.00	150.2	350.00	1450 65	1500.00	1400.23	3.00	0.80
3.	1420.75	270.0	365.23	1410.42	1460.32	1320.50	2.80	0.80
4.	1460.45	362.0	370.00	1360.55	1420.56	1300.46	2.40	0.78
5.	1500.00	472.4	380.00	1310.60	1380.50	1240.50	2.20	0.76
$Pd(DBM)_2$-I_2								
1.	540.23	11.8	380.55	785.94	770.00	730.00	2.85	0.62
2.	575.45	68.0	400.20	740.45	710.56	710.56	2.60	0.60
3.	600.30	202.0	410.46	710 55	700.20	700.23	2.40	0.58
4.	640.00	330.6	430.23	700.45	640.56	640.35	2.30	0.56
5.	700.00	405.0	440.00	685.20	610.23	610.23	2.10	0.54
$Al(DBM)_3$-I_2								
1.	850.55	14.6	310.00	—	1070.00	1040.45	—	0.70
2.	900.00	142.8	355.55	—	1000.56	990.56	—	0.68
3.	940.60	291.3	360.45	—	960.02	910.46	—	0.60
4.	1000.00	380.0	365.00	—	910.35	840.23	—	0.58
5.	1080.80	470.0	390.00	—	880.35	810.46	—	0.56

* A standard deviation of 2.0-5.0% in these values has been estimated.

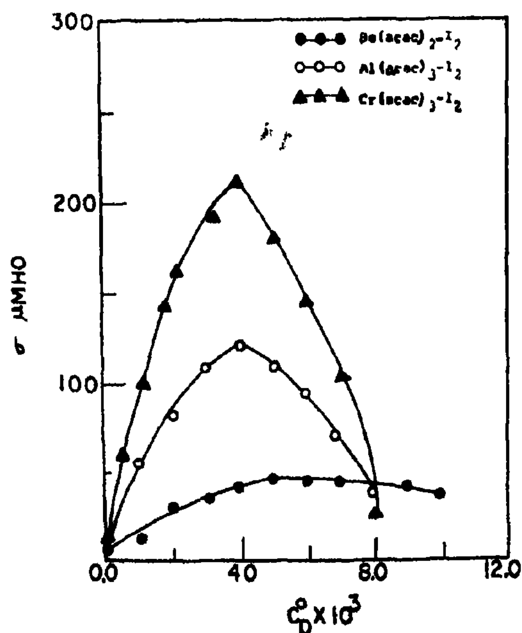


Fig. 2. Plots of molar ratio of solutes vs σ in CCl_4+CH_3CN (1 : 1) mixture for some $M(acac)_n$-I_2 complexes indicating obscured curve of $Be(acac)_2$-I_2 system and clear curve for other systems.

complex may not be fully dissociated; from the theory it follows that the dissociation constant has to be allowed for, since the carrier concentration is proportional to the concentration of M of the reagent, rather to αM, where α is the dissociation constant of the complex. A well developed conductivity maxima indicated in Fig. 2 for $Cr(acac)_3-I_2$ complex is not always obtained. In case of $Be(acac)_2-I_2$ complex, a steep sloping base line caused by serious mismatch of initial conductivities of the donor and acceptor solutions tend to yield ill-defined, or completely obscured, conductivity peak (Fig. 2). The correct stoichiometry for this case has been determined by correcting the background conductivity obtained by linear interpolation by plotting $\sigma-\sigma_0$ vs relative concentration (Fig. 3). A well developed maxima at 1 : 1 stoichiometry is thus obtained. The ill defined maxima in case of $Be(acac)_2-I_2$ complex may be due to the conductivity competition of $Be(acac)_2$ with Iodine. Since the conductivity of $Be(acac)_2$ is high compared to other $M(acac)_n$, it may create hindrance in order to get well developed maxima as has been observed in other cases. Therefore, in conductometric measurements, the correct choice of solvent is very important. If its conductivity is too high, conductance changes due to complex formation may become obscured

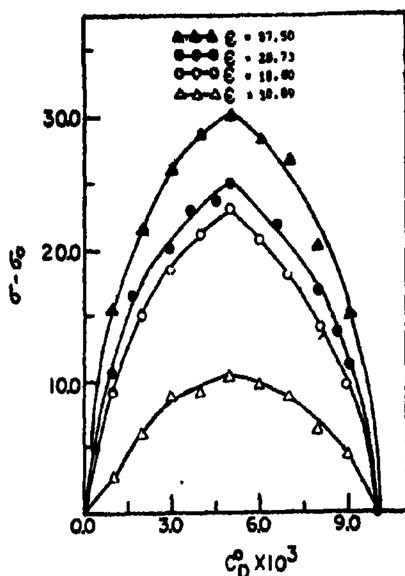


Fig. 8. Corrected stoichiometric plots of molar ratio of solutes vs $\sigma - \sigma_0$ indicating well developed maximum at 1 : 1 for $Be(acac)_2$-I_2 in the $CCl_4 + CH_3CN$ mixture of 3 : 1 (Δ—Δ—Δ), 1 : 1 (○—○—○), 1 : 3 (●—●—●) and CH_3CN (▲—▲—▼) at 30°.

and if the permittivity is too low, the complex may fail to dissociate. $Al(acac)_3$, $Al(BA)_3$, $Al(DBM)_3$ and $Fe(acac)_3$ complexes with iodine show a well developed maxima in CCl_4 but haphazard curves were noted in $CHCl_3$. Through these plots we are unable to specify the stoichiometry of these complexes. This may be due to the acceptor characteristic of $CHCl_3$ which may compete with these donors. Recently, Sahai and Badoni[16] have shown that $CHCl_3$ can be held through a weak hydrogen bond with π-electrons of pseudo-benzenoid ring of $Al(acac)_3$. In these cases by titrating $CHCl_3$ with donors in CCl_4* a well defined maxima at 1 : 1 was obtained which indicates 1 : 1 stoichiometry of the complex. In order to specify the site of interaction in $M(acac)_n$-$CHCl_3$, the conductometric titrations of benzene-$CHCl_3$ and $M(acac)_n$-$CHCl_3$ systems have been carried out in CH_3CN. It has been observed that in $M(acac)_n$-$CHCl_3$ complexes, the change in electrical conductance was greater than benzene-$CHCl_3$. systems. The σ maxima for $M(acac)_n$-I_2 systems also noted to be greater than the σ maxima for benzene-$CHCl_3$ system. This may be due to the better donor capability of $M(acac)_n$ than benzene. The presence of two CH_3 groups in these systems has made the molecule more basic than benzene. Since in both the cases of $M(acac)_n$-I_2 and benzene-I_2, the order of change in conductance is the same, the site of interaction obviously will be the same.

In order to confirm the site of interaction through refractometric studies, an equimolar solution of $Be(acac)_2$ and $CHCl_3$ (10^{-2} l. mol^{-1}) in cyclohexane were mixed, varying the volumes of donors and acceptor and keeping the total volume of the solution constant, and the refractive indices were measured. A small deviation in both the cases were noted which indicates weak interaction between donor and acceptor**. In case of $Be(acac)_2 - CHCl_3$, the $\Delta\Omega C_{DA}$ maxima was noted to be at 0.20 whereas in benzene $- CHCl_3$ it was at 0.17. This indicates that the extent of interaction in $Be(acac)_2 - CHCl_3$ is more than benzene $- CHCl_3$. This may again be interpreted as due to better donor ability of $M(acac)_n$ in $M(acac)_n - CHCl_3$ systems because of the presence of two CH_3 groups in $M(acac)_n$ as has already been described. In order to specify the site of donation in $M(acac)_n$-CCl_4 interactions, the refractometric studies have already been made[8] and it was observed that the extent of interaction is the same as was found in aromatic hydrocarbons $- CCl_4$ systems.

In case of $M(BA)_n$ and $M(DBM)_n$ systems, the doubt regarding the site of interaction becomes more as to whether the donation takes place through the π-electron pool of pseudo-benzenoid ring or through the π-electrons of the benzene ring. In these cases the donor-$CHCl_3$ interactions were studied in CH_3CN by conductometric and in cyclohexane by refractometric techniques. In both the studied, 1 : 1 complex was noted and $\Delta\Omega C_{DA}$ maxima have indicated the order of interaction : $Al(DBM)_3 > Al(BA)_3 > Al(acac)_3$. The K_1 values have also indicated the same order of interaction (Table 1.) This may be interpreted as due to better donor capability of $M(DBM)_n$ than $M(BA)_n$ and $M(acac)_n$. In $M(DBM)_n$ and $M(BA)_n$ systems, the presence of additional π-electrons have made the molecule more basic rather than the inductive effect of $-CH_3$ or $-C_6H_5$ groups. This observation clearly indicates that in metal β-diketonate-I_2 interactions, the site of interaction through the π-electron pool of the benzenoid ring cannot be ignored.

The conductivity at the conductivity peak (σ_p) of different charge-transfer complexes are listed in Table 1. From this table, it is evident that the value of σ_p increases with the increase in dielectric constant of the medium. Similar observation of σ_p with dielectric constant of the medium has been reported in case of p-phenylenediamine-picric acid complex[20]. On the basis of this observation, it can be said that the total number of ions carrying the current at the stoichiometry of the complex increases with increase in the dielectric constant of the medium. Subsequently, the complex should ionise to a greater extent in the solvent of high dielectric constant. This is in parallel agreement with our earlier observation. From Table 1, it is also evident that as soon as the dielectric constant of the medium increases, the $\Delta\Omega C_{DA}$ maxima

* Though CCl_4 also acts as electron acceptor with several hydrocarbons[17,18], compared to $CHCl_3$, it may be assumed to be inert.

** A change in electron cloud density in neutral atom or molecule will lead to a change in the polarisability. Since the complex is generally more polar than the components, the electronic polarisability or refractive index increases and the deviation depends upon the extent of interaction between donor and acceptor[8,9,11,19].

decreases. In refractometric measurements, the refraction per cm^3 due to the complex always depends upon the concentration of donor and acceptor. In the solution, the concentration of DA complex becomes low and the concentration of ionic species becomes high. This dissociation ($DA \rightleftharpoons D^+ + A^-$) depends upon the dielectric constant of the medium. Therefore, $\Delta\Omega C_{DA}$ maxima were found to be the least in CH_3CN than in CCl_4 or cyclohexane. This is because the dissociation of the complex in CH_3CN becomes maximum leaving the concentration of the complex least in the solution whereas the reverse was the case in CCl_4 and in cyclohexane. Thus we may infer upon the limitations of the conductometric and refractometric methods. In refractometric measurements, the solvent used should be of low permittivity because high permittivity of the solvent causes dissociation of the complex leading to the error in the determination of accurate and reliable value of K_1. But in conductometric measurements, the solvent should be of high permittivity which could ionise the complex as $DA \rightleftharpoons D^+ + A^-$. Thus, in order to get good results through refractometric methods, the solvent should be of low permittivity, but to get good results through conductometric methods, the solvent should be of high permittivity.

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Physico-Chemical Studies on Some Alkylmercapto- and Alkylsulphonyl Phenols

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Electric dipole moments, dissociation constants and uv absorption spectra have been determined for two alkylmercapto phenols and two alkylsulphonyl phenols. The results are examined with a view to ascertaining whether or not the 3d orbitals of the sulphur atom participate in resonance.

DESPITE extensive physicochemical investigations on a variety of organic sulphur compounds, no unequivocal conclusion has been reached regarding the participation of the 3d orbitals of the sulphur atom in resonance interaction[1]. In the case of compounds containing the bivalent sulphur atom, it has been generally observed that significant (d-p)π type of resonance interaction involving the participation of the 3d orbitals of the sulphur atom takes place in the ground state as well as in the excited state in alkyl aryl sulphides, provided a sufficiently strong electron releasing group is present *para* to the alkylmercapto group[2]. A similar conclusion has also been reached for alkyl aryl sulphones from a study of dipole moments[3], dissociatian constants[4] and uv absorption spectra[5] of a number of alkyl aryl sulphones. As part of our investigation of a large number of 4-alkylthioanilines and 4-alkylsulphonylanilines, we have found from a study of dipole moments, dissociation constants and uv absorption spectra that significant (d-p)π conjugation does take place in these types of molecules[4,6,7]. In view of the fact that the chemical reactivity of anilines and phenols are comparable, we have initiated a parallel study on 4-alkylmercapto- and 4-alkylsulphonyl-phenols with a view to finding out whether or not the hydroxyl group can enter into significant (d-p)π conjugation with the alkylmercapto and alkylsulphonyl groups. With this object in view, we have prepared two 4-alkylmercaptophenols and two 4-alkylsulphonylphenols and determined their electric dipole moments, dissociation constants and uv absorption spectra.

Experimental

All the melting points are uncorrected.

Preparation of compounds : 4-Methylmercaptophenol (1) was prepared by diazotising 4-methylthioaniline with sodium nitrite and sulphuric acid, crystallised from petroleum ether, m.p. 84-85° (lit m.p. 84-85°), yield 50%. 3-Methyl-4-methylmercaptophenol (2) was prepared in a similar manner by diazotising 3-methyl-4-methylthioaniline, crystallised from petroleum ether. m.p. 55° (lit m.p. 55-56°), yield 47%. 4-Methylsulphonylphenol (3) was prepared by oxidising 1 with 30% (by volume) hydrogen peroxide in acetic acid, crystallised from benzene, m.p. 91° (lit m.p. 91°), yield 90%. 3-Methyl-4-methylsulphonylphenol (4) was prepared in a similar manner by oxidising 2, crystallised from benzene, m.p. 103°, yield 85%. Found : C, 51.90 ; H, 5.50 ; S, 17.15%. Calcd. for $C_8H_{10}O_3S$; C, 51.61 ; H, 5.38 ; S 17.20%.

Dipole moment measurements : The dipole moments of the mercaptophenols and sulphonylphenols were determined in benzene and dioxane respectively, at 40°. The method and equipment used were the same as that reported earlier[6,7].

Dissociation constant determinations : The dissociation constants of the alkylmercaptophenols and alkylsulphonylphenols were determined by the spectrophotometric method of Robinson and Biggs[8,9]. Borax buffers were used in the case of alkylmercaptophenols and phosphate buffers were used in the case of alkylsulphonylphenols. The pK_a values obtained correspond to thermodynamic dissociation constants since the corrections for the activity coefficients of the ions have been made. The temperature of measurement was 25°.

Results and Discussion

Electric dipole moments : The electric dipole moments of the two 4-methylmercaptophenols and the two 4-methylsulphonylphenols are presented in Table 1. The dipole moments of these compounds calculated by the vector addition method are also presented in Table 1 for comparison. For the purpose of the vector addition method, the following group moments (μ_i) and group angles (θ_i) have been used : $-OH$, $\mu=1.55$ D, $\theta=90°$; $-SCH_3$, $\mu=1.34$ D, $\theta=77.5°$; $-SO_2CH_3$, $\mu=-4.73$ D, $\theta=117°$ and $-CH_3$, $\mu=0.37$ D, $\theta=0.11°$,

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TABLE 1—ELECTRIC DIPOLE MOMENTS OF 4-METHYLMERCAPTO- AND 4-METHYLSULPHONYLPHENOLS

Phenol	μObsd./D	μCalcd./D	μObsd./D–μCalcd./D
4-Methylmercapto-	2.10	2.05	0.05
3-Methyl-4-methylmercapto-	2.03	2.01	0.02
4-Methylsulphonyl-	5.70	4.97	0.73
3-Methyl-4-methylsulphonyl-	5.80	4.91	0.89

The difference between $\mu_{Obsd.}$ and $\mu_{Calcd.}$ is taken to be a measure of mesomeric interaction of the $-OH$ group with $-SCH_3$ or $-SO_2CH_3$ group, as the case may be. From the table, it is obvious that in the case of the methyl mercaptophenols the difference is negligible and hence significant (d-p)π conjugation is ruled out. On the other hand, the difference is quite considerable in the case of the methylsulphonylphenols indicating significant (d-p)π conjugation involving structure A (Fig. 1) in the ground state.

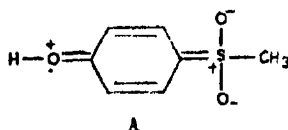


Fig 1. (d-p)π Interaction in 4 methylsulphonylphenol

Structure A involves the participation of the vacant 3d orbitals of the sulphur atom. This observation is in line with the views of Price according to whom the electron accepting properties of the sulphur atom will be prominent when the sulphur atom bears a partial positive character[12].

Dissociation constants : Dissociation constants of the two 4-methylmercaptophenols and the two 4-methylsulphonylphenols at 25° are presented in Table 2. The pK_a values for 4-methylmercaptophenol and 4-methylsulphonylphenol agree well with the values reported (9.53 and 7.89, respectively) by Bordwell and Cooper[13]. As expected, the introduction of a methyl group into the phenyl ring does not cause any significant change in the pK_a of the parent compound. Inspection of the results of Table 2 reveals the interesting fact that the acid strengthening effect of the methylsulphonyl group on the parent phenol is much greater than that of methylmercapto group (pK_a of phenol = 9.98, pK_a of *m*-cresol = 10.1 at 25°). This is again in consonance with the conclusions arrived at from dipole moment studies because resonance structures such as A will tend to increase the acidity of the phenol. Thus, the dissociation constants data also point to significant (d-p)π conjugation in the case of 4-alkylsulphonylphenols but not in the case of 4-alkylmercaptophenols.

TABLE 2—DISSOCIATION CONSTANTS OF 4-METHYLMERCAPTO- AND 4-METHYLSULPHONYLPHENOLS AT 25°

Phenol	pK_a
4-Methylmercapto-	9.61
3-Methyl-4-methylmercapto-	9.71
4-Methylsulphonyl-	7.89
3-Methyl-4-methylsulphonyl-	7.92

UV spectral data : UV absorption spectral data in 95 per cent ethanol for the four compounds studied are presented in Table 3. For two of these compounds, viz., 4-methylmercaptophenol and 4-methylsulphonylphenol, uv data have been already reported by Fehnel and Carmack[14] and our values agree well with the reported values. Further, the spectral behaviour 3-methyl-substituted phenols is virtually the same as the corresponding parent methylmercapto- and methylsulphonylphenols. In the case of the methylmercaptophenols, the uv data indicate no significant mesomeric interaction since the spectra of these compounds are not very different from those of the corresponding methylmercaptobenzenes. For methyl phenyl sulphide, for example, there are two bands – one at 254 nm (ϵ = 9550) and the other at 275 nm (ϵ = 1410). This implies that there is no significant (d-p)π conjugation in the excited state in these two compounds. On the other hand, the methylsulphonylphenols exhibit significant bathochromic shifts with reference to the corresponding methylsulphonylbenzenes. For methyl phenyl sulphone for example there are two bands – one at 217 nm (ϵ = 6760) and the other at 275 nm (ϵ = 1410). The band at 217 nm is bathochromically shifted by 23 nm and the intensity of the band increases by more than 20 times. This is indicative of (d-p)π interaction in the methylsulphonylanilines in the excited state leading to structures such as A (Fig. 1).

TABLE 3—UV SPECTRAL DATA FOR 4-METHYLMERCAPTO- AND 4-METHYLSULPHONYLPHENOLS

Phenol	λ_{max} nm	ϵ_{max}
4-Methylmercapto-	230	6920
	255	7080
	285	1070
3-Methyl-4-methylmercapto-	235	9100
	255	7580
	287	1660
4-Methylsulphonyl-	240	15850
	268	1580
3-Methyl-4-methylsulphonyl-	242	18500
	270	2000

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Kinetics and Mechanism of Oxidation of *m*-Cresol by Vanadium(V) in Presence of Salicylic and Substituted Salicylic Acids in Dilute Perchloric Acid Medium

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The kinetics of the oxidation of *m*-cresol by vanadium(V) in presence of salicylic and substituted salicylic acids was studied in perchloric acid medium. The reaction is first order each in V(V) and *m*-cresol. Plots of $1/k_1$ vs $1/[L]$ (where L represents salicylic or substituted salicylic acid) were found to be linear with positive intercepts on $1/k_1$-axes, suggesting the formation of a 1 : 1 complex between V(V) and the ligand which is believed to be a more potent oxidant. The reaction is acid-catalysed and the plot of $1/k_1$ vs $1/[H^+]$ was found to be linear with a positive intercept on $1/k_1$-axis. The applicability of Marcus theory to this reaction is discussed.

WE have recently reported the oxalic acid[1] and EDTA[2,3]-catalysed oxidations of organic and inorganic compounds by vanadium(V). The results have shown that these carboxylic acids form complexes with vanadium(V), the complexes being more potent oxidants than free V(V). While extending the study to other ligands, we found that salicylic acid catalyses the oxidation of organic compounds by vanadium(V). Recently Pelizzetti *et al*[4] applied Marcus theory to the oxidation of organic compounds by iron(III) complexes. Not much work, however, was reported in this field. Hence we have investigated the applicability of Marcus theory in the case of oxidations by V(V) complexes. For this we have investigated the kinetics of oxidation of *m*-cresol with V(V) in the presence of salicylic and substituted salicylic acids and found that Marcus correlation is valid for this vanadium(V) oxidation.

Experimental

Materials and methods : Sodium vanadate solution was prepared and standardised according to the method of Gopala Rao *et al*[5] ; *m*-cresol solution was prepared just before use and standardized bromometrically. Salicylic and sulphosalicylic acids (E. Merck, 'pro analysi') were used after recrystallization. 5-Nitro salicylic acid (m. p. 226°) was prepared by the standard method[6] and twice recrystallized. 3,5-Dibromosalicylic acid was prepared by brominating salicylic acid with liquid bromine at 10° and it was recrystallized twice from acetic acid (m. p. 180°). The purity of the compound was checked by taking the ir spectrum. All these solutions were made in glacial acetic acid. All other materials used were of AR grade.

The experiments were carried out under pseudo-first order conditions in 80% (v/v) acetic acid medium and at constant ionic strength (μ). The reaction was followed by quenching aliquots of reaction mixture at different time intervals in sulphuric acid solution containing a known excess of Fe(II) solution and the unreacted Fe(II) was titrated against standard V(V) solution using N-phenylanthranilic acid as indicator. The temperature was maintained constant to ±0.1° by Remi RK 701 ultra cryostat.

Toshniwal *p*H meter CL 46 was used to measure the redox potentials of V(V)/V(IV) couple in the presence of salicylic and substituted salicylic acids and these redox potentials were used in the Marcus plot.

Stoichiometry and product analysis : The stoichiometry of the reaction in the presence and absence of salicylic and substituted salicylic acids was found to be 2 moles of V(V) to one mole of *m*-cresol. Dienone was found to be one of the products as evidenced by spot test[7]. The stoichiometric results (Table 1) and the product analysis indicate that there is no induced oxidation by atmospheric oxygen and further, salicylic and substituted salicylic acids are not consumed through the oxidation of these ligands by V(V).

TABLE 1—STOICHIOMETRY OF THE REACTION
$[H^+] = 0.5M$; [Salicylic acid] $= 3.0 \times 10^{-3} M$,
Acetic acid = 80%(v/v) : Temp. = 25±0.1°

[V(V)] $\times 10^3 M$	[*m*-cresol] $\times 10^3 M$	$[V(V)] \times 10^3 M$ unreacted	$[V(V)] \times 10^3 M$ reacted	$\frac{[V(V)]}{[m\text{-cresol}]}$
2.0	0.30	1.39	0.61	2.03
4.0	0 40	3.21	0.79	1.98
6 0	0.50	4.98	1.02	2.04

Since *m*-cresol is known to be oxidized by V(V)[8], kinetic runs were carried out in the absence of salicylic and substituted salicylic acids. At the low temperatures and the concentrations employed in this

kinetic study, the extent of uncatalysed reaction during the time taken for following the rates of catalysed reactions has been found to be negligibly small.

Results and Discussion

The reaction is first order in V(V) as revealed by the linear plots of log[V(V)] vs time under the conditions [*m*-cresol]≫[V(V)]. Further, the pseudo-first order rate constants (k_1) are independent of the initial [V(V)] (Table 2). The pseudo-first order rate constants (k_1) at different [*m*-cresol] are presented in Table 2. It is evident from the data that the pseudo-first order rate constant k_1 is directly proportional to [*m*-cresol], indicating the first order behaviour in *m*-cresol also (Table 2).

TABLE 2—EFFECT OF VARYING [*m*-cresol], [V(V)] AND IONIC STRENGTH (μ) ON THE REACTION RATE

$[V(V)] = 2.0 \times 10^{-3} M$, [Salicylic acid] $= 1.6 \times 10^{-2} M$, $[H^+] = 0.50 M$; Acetic acid = 80% (v/v), Temp. = $10 \pm 0.1°$

10^2[*m*-cresol] *M*	$k_1 \times 10^2$ min^{-1}	$10^3 \times$ [V(V)] *M*	$k_1 \times 10^{2\varphi}$ min^{-1}	Ionic strength (μ)	$k_1 \times 10^{2\varphi}$ min^{-1}
4.0	2.28	1.0	2.30	0.50	2.28
8.0	4.59	1.5	2.21	0.75	2.23
12.0	6.80	2.0	2.28	1.00	2.12
16.0	9.01	2.5	2.26	1.25	2.42
20.0	11.6	—	—	1.50	2.35

φ at [*m*-cresol] $= 4.0 \times 10^{-2} M$.

TABLE 3—EFFECT OF VARYING [LIGAND] ON THE REACTION RATE AT DIFFERENT TEMPERATURES

$[V(V)] = 2.0 \times 10^{-3} M$, [*m*-cresol] $= 4.0 \times 10^{-2} M$, $\mu = 0.5$, $[H^+] = 0.50 M$, Acetic acid = 80% (v/v)

$10^2 \times$ [ligand], *M*	$k_1 \times 10^2$, min^{-1} at 5°	10°	15°
	Salicylic acid		
1.6	1.76	2.28	2.62
2.4	2.12	3.09	3.54
3.2	2.55	3.73	4.30
4.0	3.11	4.15	4.94
4.8	3.78	4.76	5.48
	Sulphosalicylic acid		
1.6	1.30	1.84	2.33
2.4	1.59	2.38	3.17
3.2	1.98	3.08	3.86
4.0	2.46	3.44	4.45
4.8	2.71	3.91	4.94
	5-Nitro salicylic acid		
1.6	0.89	1.38	1.84
2.4	1.20	1.95	2.51
3.2	1.41	2.38	3.07
4.0	1.68	2.81	3.55
4.8	1.79	3.03	3.96
	3,5-Dibromo salicylic acid		
1.6	2.08	2.42	2.70
2.0	2.65	3.08	3.35
2.4	2.87	3.65	4.00
2.8	3.56	4.27	4.63
3.2	4.05	4.80	5.26

Effect of varying [ligand]: The pseudo-first order rate constants, k_1, were determined at different [ligand], keeping the concentrations of the other reactants constant. Plots of $1/k_1$ vs 1/[L] were found to be linear with positive slopes and intercepts on $1/k_1$-axes (Table 3), suggesting the formation of a 1 : 1 complex between V(V) and the ligand.

Dependence on acidity: The influence of acid on the rate of oxidation has been studied and it is found that the reaction is acid-catalysed. The plot of $1/k_1$ vs $1/[H^+]$ was found to be linear with a positive intercept on $1/k_1$-axis (Table 4).

TABLE 4—EFFECT OF VARYING [ACID] ON THE REACTION RATE AT DIFFERENT TEMPERATURES

$[V(V)] = 2.0 \times 10^{-3} M$; [*m*-cresol] $= 4.0 \times 10^{-2} M$, $\mu = 0.5 M$, [ligand] $= 1.6 \times 10^{-2} M$, Acetic acid = 80% (v/v)

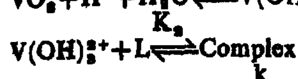
$[H^+]$ *M*	$k_1 \times 10^2$, min^{-1} at 5°	10°	15°
	Salicylic acid		
0.1	0.66	0.87	0.88
0.2	1.09	1.41	1.46
0.3	1.38	1.82	1.94
0.4	1.60	2.08	2.32
0.5	1.76	2.27	2.62
	Sulphosalicylic acid		
0.1	0.48	0.56	0.74
0.2	0.79	0.81	1.30
0.3	1.01	1.11	1.72
0.4	1.17	1.35	2.06
0.5	1.30	1.61	2.33
	5-Nitro salicylic acid		
0.1	0.34	0.50	0.58
0.2	0.55	0.84	1.01
0.3	0.70	1.09	1.35
0.4	0.81	1.31	1.62
0.5	0.89	1.38	1.84
	3,5-Dibromo salicylic acid		
0.1	0.70	0.73	0.75
0.2	1.21	1.31	1.36
0.3	1.60	1.77	1.88
0.4	1.90	2.15	2.32
0.5	2.08	2.42	2.70

Effect of ionic strength (μ): Addition of sodium perchlorate does not produce any appreciable change in the rate of the reaction (Table 2).

Rossotti and Rossotti[9] have shown that V(V) at $pH < 1$ mostly exists in the form of VO_2^+. With increasing $[H^+]$ this species is believed to be transformed into $V(OH)_3^{2+}$ [10]. Panduranga Rao and coworkers reported evidence for the formation of a 1 : 1 complex between V(V) and salicylic and sulphosalicylic acids[11,12]. In the light of these considerations, we propose that a 1 : 1 complex of V(V) and salicylic or substituted salicylic acids is formed prior to the rate-determining step, the complex being a more potent oxidant than uncomplexed V(V). The extra reactivity of this complex is presumably due to the presence of electrophilic carboxylic groups in the complex. The following scheme of mechanism accounts for all the observed kinetic results.



$$VO_2^+ + H^+ + H_2O \overset{K_1}{\rightleftharpoons} V(OH)_3^{2+}$$



$$V(OH)_3^{2+} + L \overset{K_2}{\rightleftharpoons} \text{Complex}$$



$$\text{Complex} + \text{Substrate} \xrightarrow[\text{slow}]{k} \text{Products}$$

This leads to the rate law,

$$-\frac{d[V(V)]}{dt} = \frac{k\,K_1K_2[V(V)][L][H^+][\text{Substrate}]}{1+K_1[H^+]+K_1K_2[H^+][L]}$$

Under the conditions [Sub]$\gg$[V(V)], the pseudo-first order rate constant k_1, is given by

$$k_1 = \frac{k\,K_1K_2[L][H^+][\text{Substrate}]}{1+K_1[H^+]+K_1K_2[H^+][L]}$$

Hence,

$$\frac{1}{k_1} = \frac{1}{k\,K_1K_2[L][H^+][\text{Sub}]} + \frac{1}{k\,K_2[L][\text{Sub}]} + \frac{1}{k\,[\text{Sub}]}$$

Thus the plots of $1/k_1$ vs $1/[L]$ and $1/k_1$ vs $1/[H^+]$ should be straight lines with positive slopes and intercepts. This has actually been observed providing kinetic evidence for the complex formation between vanadium(V) and salicylic or substituted salicylic acids. This type of acid dependence in V(V) oxidations has been reported earlier by us[1] and by Sengupta *et al*[13].

From the slopes and intercepts of the plots mentioned above, the values of k, K_1, K_2 were calculated and are presented in Tables 5 and 6. From the rate data, the activation parameters have been determined and these results are listed in Table 5.

TABLE 5—THE VALUES OF SPECIFIC RATE CONSTANTS (k) AND ACTIVATION PARAMETERS

Ligand	k lit. mol^{-1}min^{-1} at 5°	10°	15°	$E_a^{\neq}$ K.cal mol^{-1}	$-\Delta S^{\neq}$ cal deg^{-1} mol^{-1}
Salicylic acid	2.08	2.56	3.02	6.40	35.8
Sulpho salicylic acid	1.85	2.37	2.81	7.71	31.4
5-Nitro salicylic acid	1.00	1.66	2.34	15.91	3.1
3,5-Dibromo salicylic acid	10.00	16.66	25.70	1.59	50.0

According to Marcus[14] the free energy of activation $\Delta G^{\neq}$ for an outer-sphere electron-transfer reaction is related to the overall free energy change, ΔG, of the reaction by the relation

$$\Delta G^{\neq} = \lambda/4\,(1+\Delta G/\lambda)^2 \qquad \ldots (1)$$

where λ is a parameter related to the reorganization of the inner and outer coordination spheres of the reacting complex. If the reorganization term λ is $\gg \Delta G$, the quadratic term drops out and the equation (1) simplifies[15] to

$$\Delta G^{\neq} = \lambda/4 + 0.5\Delta G \qquad \ldots (2)$$

Since the overall free energy change ΔG is proportional to the difference in the redox potentials of oxidizing and reducing couples, (E_2 and E_1 respectively) and $\Delta G^{\neq}$ is proportional to log k, equation (2) changes to[16]

$$\log k = 8.5(E_2 - E_1) + \text{constant} \qquad \ldots (3)$$

For a series of substituted ligands and for the same reductant (λ and E_1 are constant) the equation assumes the form

$$\log k = 8.5\,E_2 + \text{constant} \qquad \ldots (4)$$

where E_2 is the redox potential of the oxidizing couple. Subsequently, Marcus has reported that this correlation is also valid for redox reactions proceeding via inner-sphere mechanisms[17]. Thus, for closely related ligands, log (rate constant) must be linearly related to redox potential E_2 of the oxidizing couple with theoretical slope equal to 8.5.

To test the validity of this correlation, we determined the rate constant k (as defined in the mechanism) and also the redox potential of the oxidizing couple, V(V)/V(IV), in the presence of salicylic and substituted salicylic acids which form complexes with vanadium(V) and found that log k is linearly related to the redox potential of V(V)/V(IV) couple with a slope equal to 9 which is in fair agreement with the theoretical slope of 8.5. (Fig. 1). This shows the applicability of Marcus theory for the present reaction.

Recently, Pelizzetti *et al* have verified this correlation in organic oxidations by metal complexes[4,18]. This correlation has also been tested in a number of electron-transfer reactions between metal complexes proceeding via both inner[19,20] and outer-sphere[21] mechanisms.

TABLE 6—THE VALUES OF K_1, K_2 AND THERMODYNAMIC PARAMETERS

Ligand	K_1M^{-1} 5°	10°	15°	(ΔH) K.cal/mole	K_2, M^{-1} 5°	10°	15°	(ΔH) K.cal/mole
Salicylic acid	1.82	1.32	0.97		35.2	44.9	58.0	8.22
Sulpho salicylic acid	1.80	1.27	0.99	−12.54	27.9	36.3	50.1	11.97
5-Nitro salicylic acid	1.81	1.41	1.02		37.5	42.9	46.7	5.70
3,5-Dibromo salicylic acid	1.84	1.38	0.95		7.2	6.0	5.2	7.14

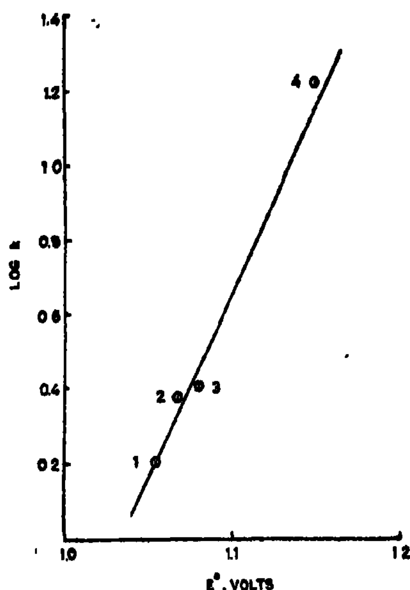


Fig. 1. Relationship between the logarithms of the specific rate constant for the oxidation of *m*-cresol by different V(V)-ligand complexes (10°, μ=0.50*M*) and the formal redox potential of V(V)/V(IV) couple in the presence of salicylic and substituted salicylic acids
(1) 5-Nitrosalicylic acid
(2) Sulphosalicylic acid
(3) Salicylic acid
(4) 3,5-Dibromosalicylic acid.

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Kinetic Study of Ag(I) Catalysed Oxidation of Glycine by Ce(IV) in Perchloric Acid Medium

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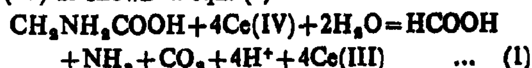
The kinetics of Ag(I) catalysed oxidation of glycine by ceric perchlorate in perchloric acid solution are reported. The reaction follows first-order kinetics with respect to each Ce(IV), glycine and perchloric acid. The reaction rate is found to be accelerated by Ag(I). Formic acid and ammonia are found to be reaction products. A suitable mechanism involving formation of a transient complex [glycine-Ce(IV)] has been proposed.

ERIC salts in various acidic solutions have been widely utilised for the oxidation of organic as well as inorganic compounds[1-8]. In some cases he mechanistic approach has been based on the ntermediate complex formation and in others the esults have been interpreted by free radical mechaism in absence of kinetic or spectrophotometric vidence. Sometimes anionic species present in the eaction have also been considered responsible for eciding the cationic species of Ce(IV). Oxidation f some aliphatic acids such as formic acid[9], lactic cid[8] and acetic acid[10] was studied by using ceric erchlorate only as an oxidant. The mechanism uggested by various authors is not uniform, indicang that wide varieties of mechanism are possible epending upon the nature of cationic species as ell as substrates and any inference made on nalogy would be naive. In this paper, we report he results and mechanism of oxidation of glycine y ceric perchlorate in perchloric acid medium in resence of Ag(I) as catalyst on the basis of product stimation and spectrophotometric evidence for the omplex formation between glycine and Ce(IV).

Materials and method: The stock solution of eric perchlorate was prepared by dissolving ceric mmonium nitrate A. R. (B. D. H.) in aqueous erchloric acid (Riedel, 60%). The acid strength f the stock solution was determined by McAuley's ethod[11]. The stock solution of glycine (E. Merck) was prepared by weighing and dissolving in distilled ater. Other reagents were sodium perchlorate Riedel), sodium hydroxide A. R. (B. D. H.), errous ammonium sulphate A. R. (B. D. H.) and erroin indicator (E. Merck).

The solutions of reactants were kept in a thermostatic bath to attain thermal equilibrium. The required amount of reactants were mixed together and aliquot (5.00 ml) was withdrawn from the mixture at different intervals of time and was added to a known volume of ferrous ammonium sulphate solution. The excess of ferrous was titrated with a standard solution of ceric sulphate using ferroin as an indicator. The kinetic runs were studied using excess of glycine in the reaction mixture and the value of first order rate constant (k_1) was calculated by using the first order rate expression.

Stoichiometry and product analysis: A number of reaction mixture containing a known excess of ceric perchlorate over glycine was kept at 40° at 2*M* $HClO_4$. The amount of Ce(IV) left revealed 1 : 4 stoichiometry (Table 1) between glycine and Ce(IV) as shown in eqn. (1).



$$CH_2NH_2COOH + 4Ce(IV) + 2H_2O = HCOOH + NH_3 + CO_2 + 4H^+ + 4Ce(III) \quad \ldots (1)$$

The product formic acid was identified by ascending paper chromatography using *n*-butanol with ammonia as solvent system and bromo-phenol blue as spot revealing reagent. The R_f value was found to be 0.50.

TABLE 1—TEMPERATURE 40°±0.1

[Ceric perchlorate] × 10^3*N*	[Glycine] × 10^4*M*	[Ce(IV)]/[Glycine]
1.00	1.50	3.96
2.00	1.50	4.00
2.56	1.50	4.04
3.00	1.50	4.12

Average value of equivalent = 4.03

Results and Discussion

The glycine-Ce(IV) oxidation was studied at several initial [reactants]. It was observed that the reaction follows first order kinetics in Ce(IV) which is obvious from the kinetic runs (Tables 2A and 2B). Contrary to our expectation the reaction rate decreases with increasing Ce(IV) concentration (Table 3). The unusual trend may be attributed to the formation of some unreactive polymeric ceric species at higher concentrations as suggested by Hardwick and Robertson[12] in high perchloric acid solutions.

The rate dependence of the reaction on glycine indicates first order. The rate of reaction increases

* For correspondence.

TABLE 2A—TEMPERATURE 40°±0.1

[Ceric perchlorate] = $4.00 \times 10^{-3} M$
[Glycine] = $10.00 \times 10^{-3} M$
[$AgNO_3$] = $1.00 \times 10^{-3} M$
[$HClO_4$] = 2.00M

$\mu = 2.56M$ (Adjusted by adding suitable amounts of sodium perchlorate solution).

Time (min)	ml of $3.84 \times 10^{-3} N$ $Ce(SO_4)_2$ required by 5 ml of the reaction mixture	$k_1 \times 10^3$ min^{-1}
0	1.84	—
10	2.18	5.88
20	2.52	5.55
30	2.82	5.49
45	3.28	5.58
60	3.66	5.45
80	4.14	5.65
100	4.58	5.52
120	4.98	5.49
150	5.48	5.40
T_∞	8.30	—

Average value of $k_1 \times 10^3 = 5.56$ min^{-1}
Average deviation = ±1.18%

TABLE 2B—TEMPERATURE 45°±0.1

[Ceric perchlorate] = $4.00 \times 10^{-3} M$
[Glycine] = $10.00 \times 10^{-3} M$
[$AgNO_3$] = $1.00 \times 10^{-3} M$
[$HClO_4$] = 2.00M

$\mu = 2.56M$ (Adjusted by adding suitable amounts of sodium perchlorate solution).

Time (min)	ml of $3.84 \times 10^{-3} N$ $Ce(SO_4)_2$ required by 5 ml of the reaction mixture	$k_1 \times 10^3$ min^{-1}
0	1.84	—
10	2.34	8.05
20	2.80	8.03
30	3.22	8.08
45	3.80	8.00
60	4.32	7.98
75	4.76	8.02
90	5.16	7.66
105	5.52	8.02
120	5.84	6.98
T_∞	8.30	—

Average value of $k_1 \times 10^3 = 7.97$ min^{-1}
Average deviation = ±0.50%

TABLE 3—EFFECT OF VARIATION OF [CERIC PERCHLORATE] ON THE RATE OF REACTION

Temperature 40°±0.1, [Glycine] = $10.00 \times 10^{-3} M$,

[$AgNO_3$] = $1.00 \times 10^{-3} N$ and [$HClO_4$] = 2.00N, $\mu = 2.56M$ (Adjusted by addition of suitable amounts of sodium perchlorate solution)

[Ceric perchlorate] $\times 10^3 N$	1.00	1.25	1.67	2.00	2.50	4.00	5.00
$k_1 \times 10^3$ min^{-1}	16.04	12.45	11.86	9.78	7.54	5.53	4.49

on increasing the concentration of glycine and has direct proportionality (Table 4).

The rate of the reaction increases with the increase in [H^+] and have direct proportionality. The values of second order rate constant i.e. k_2 (k_1/[$HClO_4$]) shown in 4th column of Table 4 are almost constant showing first order dependence of the reaction on perchloric acid.

TABLE 4—EFFECT OF VARIATION OF TEMPERATURE, [GLYCINE] AND [$HClO_4$] ON THE RATE OF THE REACTION AT IONIC STRENGTH $\mu = 2.56M$ (ADJUSTED BY ADDITION OF SUITABLE AMOUNTS OF SODIUM PERCHLORATE SOLUTION)

Temp. °C	[Glycine] $\times 10^3 M$	[$HClO_4$] M	$k_1 \times 10^3$ min^{-1}	$k_2 \times 10^3 = (k_1$/[Glycine] or [$HClO_4$]) l mole^{-1} min^{-1}
40	5.00	2.00	4.62	9.20
40	7.50	2.00	6.82	9.00
40	10.00	2.09	9.78	9.78
40	12.50	2.00	12.02	9.60
40	15.00	2.00	14.68	9.70
40	20.00	2.00	18.72	9.36
40	10.00	0.75	3.80	5.06
40	10.00	1.00	5.19	5.19
40	10.00	1.25	6.38	5.10
40	10.00	1.50	8.34	5.56
40	10.00	2.00	9.78	4.89
40	10.00	2.50	12.87	5.15
40*	10.00	2.00	5.50	—
45*	10.00	2.00	7.97	—
50*	10.00	2.00	12.37	—
55*	10.00	2.00	16.98	—

* [Ceric perchlorate] = $4.00 \times 10^{-3} M$.

In absence of Ag(I) ions, the reaction between glycine and ceric perchlorate is too slow to be measured. The effect of variation of [Ag^+] ions on reaction rate is given in Table 5. Though no relationship is established between [Ag(I)] and k_1 values, the reaction rate is accelerated on increasing silver nitrate concentration. Measurements were made at 40, 45, 50 and 55° to investigate the temperature effect (Table 4). The energy of activation was evaluated from the Arrhenius plots as 15.10 ± 0.05 k.cal mol^{-1}. The entropy of activation was calculated and found to be −18.26 e.u. The variation in ionic strength (μ) of the medium, (adjusted by addition of suitable amounts of sodium perchlorate solution), showed positive effect on the reaction rate (Table 5). This indicates interaction between two similarly charged species.

TABLE 5—EFFECT OF VARIATION OF [SILVER NITRATE] AND IONIC STRENGTH (μ) OF THE MEDIUM ON THE RATE OF REACTION AT 40°±0.1°

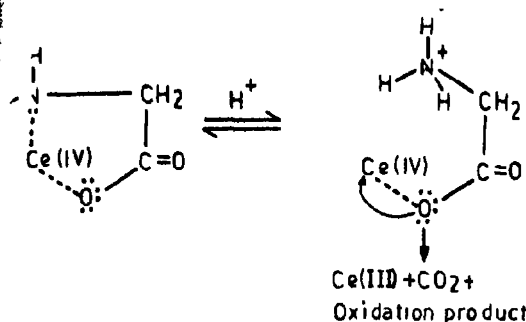
[Ceric perchlorate] = $2.00 \times 10^{-3} M$, [$HClO_4$] = 2.00M and [Glycine] = $10.00 \times 10^{-3} M$

[$AgNO_3$] $\times 10^4 M$	Ionic strength (μ)* M	$k_1 \times 10^3$ min^{-1}
4.00	2.56	6.38
5.00	2.56	6.94
6.70	2.56	8.16
8.00	2.56	8.72
10.00	2.56	9.78
12.50	2.56	12.74
10.00	2.08	7.84
10.00	2.75	10.68
10.00	3.25	17.90
10.00	3.52	20.80
10.00	4.02	23.62
10.00	4.50	27.52

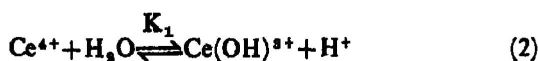
* Variation in μ was affected by adding suitable amounts of sodium perchlorate solution.

The increase in rate with increasing acidity may be explained generally in terms of a model which

trays the Ce(IV) co-ordinated by both N and boxylate ligands. The quality of Ce(IV) as an etron sink is not fully sensed by the carboxylate long as the electron pair of the N ligand occupies of the positions available around the metal ion. ith increasing acidity, H^+ competes with Ce(IV) an electron pair acceptor and when N is protonted, the Ce(IV) character as an electron sink is hanced and electron transfer from a co-ordinated rboxylate takes place.



The rate vs acidity reaction profiles observed in this work may be explained in terms of mechanistic pathways involving certain active species whose concentrations are controlled by the acidity of the medium. The main species[12-16] in $HClO_4$ are unhydrolysed $[Ce(H_2O)_8^{4+}]$, the hydrolysed $[Ce(OH)(H_2O)_7^{3+}]$ and $[Ce(OH)_2(H_2O)_6^{2+}]$. Although evidence for dimeric species, e.g. $(Ce-O-Ce)^{6+}$, $(HOCe-O-CeOH)^{6+}$ etc. has been given[16] depending upon the acid concentration in solutions which have less than $1\times10^{-3}M$ Ce(IV), their importance can be ignored as the predominant species is monomeric[17] in the perchloric acid concentration range 0.2-2.0 *M*. The concentrations of various species of Ce(IV) which may exist in $HClO_4$ are governed by the following equilibria.


$$Ce^{4+}+H_2O \overset{K_1}{\rightleftharpoons} Ce(OH)^{3+}+H^+ \quad (2)$$


$$Ce(OH)^{3+}+H_2O \overset{K_2}{\rightleftharpoons} Ce(OH)_2^{2+}+H^+ \quad (3)$$

The latest values of K_1 and K_2 are 6.4 and 0.12 respectively[18]. In calculating the fraction of Ce(IV) which exists as the unhydrolysed species at a particular $[H^+]$, use is made of the above equilibrium constant. Thus,

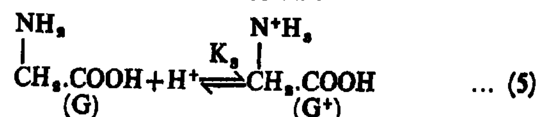
$$\frac{1}{{}^{s}Ce^{4+}} = 1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2} \quad \ldots (4)$$

where ${}^{s}Ce^{4+}$ refers to the unhydrolysed Ce^{4+} species. Computations according to eqn. (4)[18] show that ${}^{s}Ce^{4+}$ increases with acidity in $HClO_4$ solutions (Table 6). This unhydrolysed species is probably the most active Ce(IV) species in the reported conditions of the reaction medium and an increase in the acid concentration would lead to an increase in the observed rate.

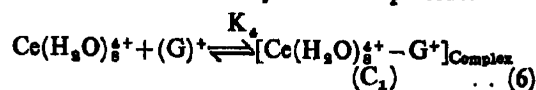
TABLE 6—CONCENTRATION DISTRIBUTION OF Ce(IV) SPECIES AT DIFFERENT ACIDITIES

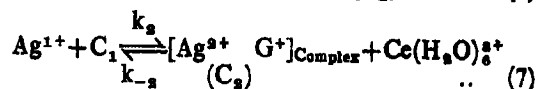
$[H^+]$	${}^{s}Ce^{4+}$	${}^{s}Ce(OH)^{3+}$
0.6	0.072	0.778
1.0	0.122	0.782
2.0	0.227	0.720
3.0	0.310	0.661
4 0	0.377	0.600
5.0	0.432	0.548

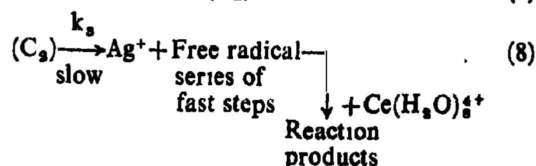
In acid solutions glycine will be protonated and can be shown to exist as below :


$$\underset{(G)}{NH_2CH_2.COOH}+H^+ \overset{K_3}{\rightleftharpoons} \underset{(G^+)}{N^+H_3CH_2.COOH} \quad \ldots (5)$$

The most satisfactory reaction mechanism best fitting our kinetic data may thus be represented as


$$Ce(H_2O)_8^{4+}+(G)^+ \overset{K_4}{\rightleftharpoons} \underset{(C_1)}{[Ce(H_2O)_8^{4+}-G^+]_{Complex}} \quad \ldots (6)$$


$$Ag^{1+}+C_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(C_2)}{[Ag^{2+}\ G^+]_{Complex}}+Ce(H_2O)_8^{3+} \quad \ldots (7)$$


$$(C_2)\xrightarrow[\text{slow}]{k_3}Ag^++\text{Free radical}\xrightarrow{\text{series of fast steps}}+Ce(H_2O)_8^{3+}\ \text{Reaction products} \quad (8)$$

Ag^+ reacts with complex (C_1) *to form another* complex (C_2) of bivalent silver, which decomposes to give Ag^+ and free radical.

Eqn. (8) is rate determining step. Applying the steady state condition with respect to C_2 (complex), we derive the rate law eqn. (9) from the steps 5-8, where $k_3 \gg k_{-2}[Ce(H_2O)_8^{3+}]$ $\frac{-d[Ce(IV)]}{dt}=k_2K_3K_4$ $[Ce(H_2O)_8^{4+}][Glycine][H^+][Ag^+]$

or rate $=k_2K_3K_4[Ceric][Glycine][HClO_4][Ag^+]$ .. (9)

At constant $[Ag^+]$, eqn. (9) is expressed as

rate $=k_4[Ceric][Glycine][HClO_4]$. (10)

where $k_4=k_2K_3K_4[Ag^+]$

This eqn. (10) is in complete accord with the observations.

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Flow Through Porous Medium. Part-VI : Permeability Studies of Water and Ammonium Salt Solutions Through Soil Membrane

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The phenomenological permeation coefficients for water and aqueous solutions of ammonium nitrate, ammonium sulphate, ammonium phosphate at different concentrations and at 35° were determined for a soil membrane of known thickness and water content. The results have been interpreted in terms of the principles of non-equilibrium thermodynamics. It has been found that the permeation coefficient for water is higher than that of the ammonium salt solutions. Frictional coefficient between membrane matrix and water has been evaluated and its dependence upon the solute concentration has also been discussed. The effect of concentration of the electrolyte solution on the radius of pore of the membrane equilibrated with the electrolyte solution has also been discussed.

STUDIES involving electrolyte and non-electrolyte solutions have been made by a number of investigators[1-7] on transport through different types of diaphragms, both theoretically and experimentally, from different angles using thermodynamics of irreversible processes. But a survey of literature shows that the application of irreversible thermodynamics to the rate processes encountered in soil systems is only of recent origin. Flow through soil membranes has been actively studied because of their importance in various processes such as nutrient movement, desalination, leaching, soil stabilization etc. These transport processes not only characterise[8] the membrane in terms of its effective cross-sectional area, radius and number of pores but also characterise the system as a whole in terms of a set of experimentally accessible phenomenological coefficients. Moreover, these processes help us to elucidate the structure[6] of compounds by determining permeant-permeant and membrane-permeant interactions estimated from the excess values of these phenomenological coefficients[7]. Spiegler[9] made an attempt to translate the phenomenological permeation coefficients, used in the thermodynamic description of permeation through membranes, into frictional terms and this approach was extended by Kedem and Katchalsky[10], who derived a set of equations in which the phenomenological permeation coefficients are expressed as explicit functions of frictional coefficients as well as of some membrane characteristics such as membrane thickness, water content and tortuosity of capillaries. The present investigations have been carried out with a soil membrane using different liquids in order to test the validity of the theory of thermodynamics of irreversible process in soil systems.

Experimental

Electrolytes : Ammonium nitrate, ammonium sulphate and ammonium phosphate were used in the present investigations. The electrolytes were of G.R. grade and were used as such without further purification after drying over calcium chloride in a vacuum desiccator. Distilled water, distilled thrice over alkaline $KMnO_4$, was used in the present investigations. The conductivity of the water so prepared was of the order of 10^{-6} ohm^{-1} cm^{-1}.

Membrane : Known amounts (8 g) of soil, collected from Simla Hills at a height of 7000 ft above mean sea level in Himachal Pradesh, were supported in a burette. Conductivity water was then allowed to percolate through the column of the soil for a number of days in order to remove washable impurities. After this, the soil was dried in vacuum oven at 100° and transferred to the apparatus (Fig. 1). Here the soil was supported over a glass wool plug. Now the soil was pressed mechanically with the help of a glass rod flattened at the ends. A glass wool pad was then placed at the top of the bed of the soil. Conductivity water was allowed to pass through the soil until constant flow rate was observed in the capillary tube of the apparatus. The constant flow was obtained after a lapse of four days. This is natural because clay is smectitic and, therefore, the soil sample swells on treatment with water and the aqueous salt solution used. The membrane so prepared was 3 cm in thickness and 1.83 cm in diameter.

Apparatus and methods : The apparatus used for this purpose is depicted in Fig. 1. It consists of a 6 cm long pyrex glass tube A having a standard female joint B at its upper end and a standard male joint C at its lower end. A capillary tube D is sealed at the joint C, whereas a reservoir R is connected to the joint B through a polythene tube T having a standard male joint E at its lower end. The reservoir is movable and can be set at any position to maintain the desired pressure gradient in the system. The whole apparatus was kept in a thermostat and all the measurements were made

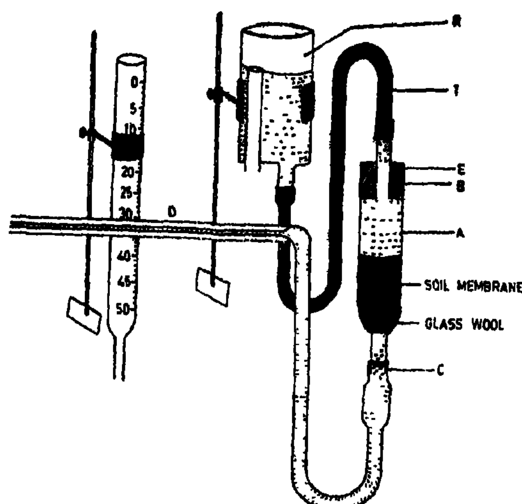


Fig. 1. Apparatus for the measurement of hydrodynamic permeability.

at 35°. The temperature was kept constant with the help of a toluene-mercury thermoregulator and an electronic relay.

To measure the flow of water due to a pressure gradient across the membrane, the apparatus was filled with conductivity water and was kept as such overnight so as to saturate the soil membrane completely. Now a constant known magnitude of pressure gradient, say 10 cm, was imposed by maintaining a constant difference in the level of the liquid across it. The ensuing hydrodynamic volumetric flux was measured by following the displacement of the liquid meniscus in the horizontally placed graduated capillary tube with the help of a cathetometer sensitive to 0.001 cm. The time was recorded with the help of a stopwatch reading correctly up to 0.1 second. Changes in the volumetric flux of the liquid were determined correct to 0.48 microlitre by observing the level of liquid in the capillary tube with the help of the cathetometer. The reading was repeated four times and the mean value of the volumetric flux was calculated. Now the experiment was performed at other pressure gradients say 15, 20, 25 and 30 cm of the permeant across the membrane. Measurements of volumetric flux through the membrane for various electrolyte solutions of different concentrations at different pressure differences were also made. Densities of different solutions were determined with the help of a bicapillary pycnometer.

Conductance of the membrane and the specific conductivity of the permeant were determined by means of a Toshniwal conductivity bridge at 50 cycles/sec. Viscosities of the ammonium salt solutions were determined by the suspended level type viscometer.

Results and Discussion

According to the theory of thermodynamics of irreversible processes, the dissipation function, ϕ, for the transport process through a membrane under the simultaneous action of the gradients of pressure and concentration is given by Lakshminarayanaiah[11] :

$$\phi = J_V \Delta P + J_D \Delta \pi \quad \ldots (1)$$

where J_V is the volumetric flux ; J_D, the relative velocity of solute to that of solvent and bears a similarity to the ordinary diffusional flux. ΔP and $\Delta \pi$ are the pressure and concentration gradients respectively across the membrane.

The phenomenological equations relating the flows and forces defined by relation (1) are :

$$J_V = L_P \Delta P + L_{PD} \Delta \pi \quad (2)$$

$$J_D = L_{DP} \Delta P + L_D \Delta \pi \quad \ldots (3)$$

L_P, L_{PD}, L_{DP} and L_D are the phenomenological coefficients and represent the different properties of the membrane.

For this system, the Onsager's reciprocity relationship is

$$L_{PD} = L_{DP} \quad . (4)$$

The significance of relations (2) and (3) can be tested by the examination of different physical situations. Let us consider an experiment in which the concentration of the solute is the same on both the sides of the membrane, so that $\Delta \pi = 0$. If a pressure gradient is maintained, there will exist a volume flow, J_V. The values of volume flow of water and aqueous solutions of ammonium salts through the soil membrane are recorded in Tables 1 and 2 respectively.

TABLE 1—PERMEABILITY DATA FOR WATER AT DIFFERENT PRESSURE DIFFERENCES AND AT 35°

ΔP (cm of permeant)	$J_V \times 10^4$ (cm. sec^{-1})
10	1.21
15	1.55
20	1.95
25	2.48
30	2.98

When the concentration of the solute is the same on both the sides of the membrane the volume flow, J_V, will be given as :

$$J_V = L_P \Delta P \quad \ldots (5)$$

where L_P is the permeability of the membrane for the fluid. L_P has a character of mobility and represents the velocity of fluid through the membrane per unit pressure difference across the membrane. The values of L_P for water and ammonium salt solutions have been estimated from the plots between J_V and ΔP and recorded in Table 3. The plots representing the variation of J_V with ΔP for different fluids are given in Fig. 2.

TABLE 2—PERMEABILITY DATA OF DIFFERENT AMMONIUM SALT SOLUTIONS OF DIFFERENT CONCENTRATIONS AT DIFFERENT PRESSURE DIFFERENCES AND AT 35°

ΔP	$J_v \times 10^4$ (cm. sec^{-1})					
(cm. of permeant)	0.005*M*	0.01*M*	0.02*M*	0.04*M*	0.06*M*	0.08*M*
			Ammonium nitrate			
10	0.64	0.58	0.55	0.58	0.51	0.49
15	0.96	0.88	0.78	0.78	0.72	0.67
20	1.35	1.01	0.96	0.88	0.84	0.82
25	1.74	1.24	1.16	1.09	1.02	0.99
30	2.56	1.67	1.54	1.41	1.31	1.24
			Ammonium sulphate			
10	0 60	0.51	0.49	0.47	0.46	0.44
15	0.87	0.69	0 65	0.62	0.59	0.56
20	1.15	0.94	0.86	0.82	0.77	0.73
25	1.49	1.21	1.11	1.06	1.01	0.97
30	1.98	1.50	1.42	1.32	1.22	1.14
			Ammonium phosphate			
10	0.47	0.44	0.43	0.41	0.40	0.39
15	0.79	0.62	0 57	0 55	0 54	0.53
20	1.02	0.89	0.84	0 81	0.79	0 76
25	1.25	1 09	1.08	1.06	1.02	0 97
30	1 43	1.36	1 25	1.21	1.19	1.11

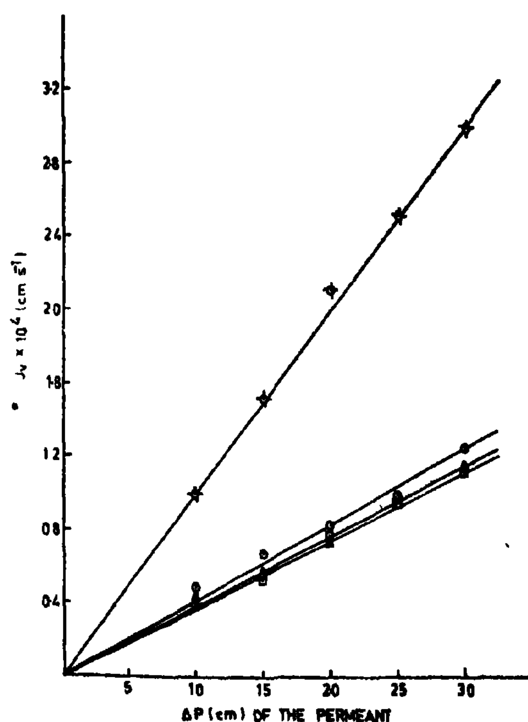


Fig 2. Variation of J_v with ΔP at 35°.
—⊗—⊗—Water
—○—○—0.08*M* Ammonium nitrate solution
—△—△—0.08*M* Ammonium sulphate solution
—▣—▣—0 08*M* Ammonium phosphate solution

Table 3 shows that the filtration coefficient decreases as one goes from NH_4NO_3 to $(NH_4)_3PO_4$.

TABLE 3—MECHANICAL FILTRATION COEFFICIENT, L_p, OF SOIL MEMBRANE FOR WATER AND AMMONIUM SALT SOLUTIONS AT DIFFERENT CONCENTRATIONS AND AT 35°

Concentration (mol. l^{-1})	$L_p \times 10^8$ (cm^3.S^{-1}.dyn^{-1})		
Water		1.025	
Salt	NH_4NO_3	$(NH_4)_2SO_4$	$(NH_4)_3PO_4$
0 005	0.72	0.61	0.51
0 01	0 58	0.49	0.47
0.02	0.53	0.46	0.44
0.04	0.48	0.43	0.43
0 06	0.45	0.41	0.41
0.08	0.43	0.39	0.38

This decrease is attributed[12] to the increase in the radii of the anions namely, PO_4''' (2.38 Å) > SO_4'' (2.30 Å) > NO_3' (1.89 Å). From Table 3 it is evident that the permeability of the different fluids at 35° through the soil membrane varies in the order :



$$H_2O > NH_4NO_3 > (NH_4)_2SO_4 > (NH_4)_3PO_4$$

On translating the thermodynamic coefficients into frictional coefficients, it has been found that L_P can be related to the coefficient of friction between water and the membrane matrix, f_{wm}, by the relation[13] :

$$L_P = \frac{\phi_w \bar{V}_w}{f_{wm} \delta} \quad \ldots (6)$$

where ϕ_w is the water content of the wet membrane and is expressed as the volume fraction of water of the total membrane volume. It is numerically identical with the fraction of the membrane surface available for the premeation of water-soluble substances[14] and plays an important role in subsequent calculations. The volume fraction of water of the membrane is its characteristics and has been determined in the present case by the method described by Ginzburg and Katchalsky[14]. $\bar{V}_w$ is the partial molar volume of water and δ is the thickness of the membrane. Substituting the values of ϕ_w, $\bar{V}_w$, L_P and δ for the membrane, f_{wm} can be calculated using eq. (6). The values of the frictional coefficient, f_{wm}, of the membrane for different fluids used in the present study are given in Table 4.

TABLE 4—FRICTIONAL COEFFICIENT, f_{wm}, FOR WATER AND AMMONIUM SALT SOLUTIONS AT DIFFERENT CONCENTRATIONS AND AT 35°

Concentration (mol. l^{-1})	$f_{wm} \times 10^{-8}$ (dyn. sec. cm^{-1}. mol^{-1})		
Water		3.46	
Salt	NH_4NO_3	$(NH_4)_2SO_4$	$(NH_4)_3PO_4$
0.005	4.88	5.75	6.89
0.01	6.03	7 05	7.51
0.02	6.57	7.66	7.89
0 04	7.26	8.12	8.24
0.06	7.76	8.49	8.64
0 08	8.18	8.95	9.14

Table 4 shows that the value of f_{wm} when pure water flows, is less than that of f_{wm} when electrolyte

solution flows through the membrane. It is inferred from this that the resistance offered by the soil to water in its penetration through the membrane is less than that offered to the electrolyte solution. The variation of f_{wm} with salt concentration is shown in Fig. 3. The figure shows that at higher concentration of the electrolyte f_{wm} tends to become independent of concentration.

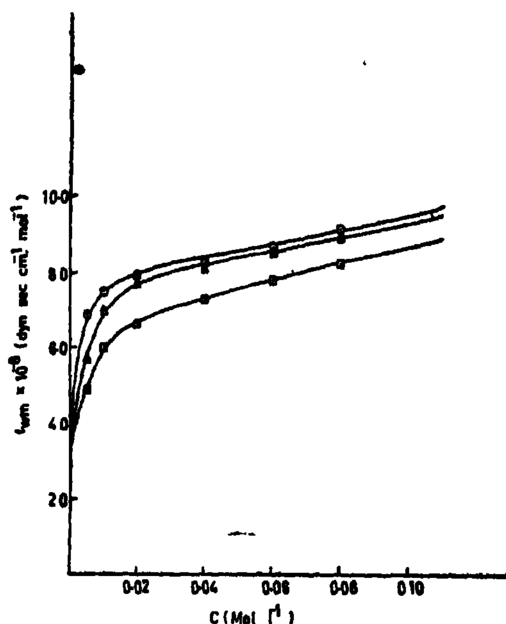


Fig. 3. Dependence of f_{wm} upon concentration of the electrolyte at 35°.

—○—○—Ammonium phosphate
—△—△—Ammonium sulphate
—⊡—⊡—Ammonium nitrate

Evaluation of the average porosity of the soil membrane : The complex nature of the membrane porosity is due to the absence of straight capillaries. The liquid flows in a zig-zag path and the characterization of such a membrane is possible only in terms of $\frac{A}{l}$ from which the average porosity can be estimated. Under the action of the hydrostatic pressure or the electrical current, the rate of permeation will depend on the effective cross-sectional area A and the thickness of the membrane l. Because of the complex nature of the openings inside the membrane, it is not possible to determine the values of the above mentioned quantities. However, $\frac{A}{l}$, the membrane constant can be determined, in terms of which the permeation behaviour of any soil membrane can be expressed.

Now consider a membrane having n number of pores of equivalent radius 'r' and effective length l. The effective cross-sectional area A of this membrane through which permeation occurs can be equated to

$$A = n\pi r^2$$

If k is the specific conductivity of the permeant, then the electrical conductance of the permeant can be written as[8] :

$$K = \frac{n\pi r^2 k}{l} \quad \text{(7)}$$

$$= \frac{A}{l} \cdot k \quad \text{... (8)}$$

Hence the membrane constant $\frac{A}{l} = \frac{K}{k}$ ... (9)

where K is the conductance of the membrane plus the solution, and k is the specific conductance of the solution determined by the usual conductivity measurements.

The membrane constant characterises the membrane but does not depend on the nature of the permeating solution, so long as the interaction between the permeant and membrane matrix is negligible and is not in a position to change the equivalent pore radius.

The values of the membrane constant obtained from the conductance data of different ammonium salt solutions are given in Table 5.

TABLE 5—MEMBRANE CHARACTERISTICS OBTAINED FROM THE CONDUCTANCE MEASUREMENTS

Concentration (mol. l^{-1})	$K \times 10^4$ (mhos)	$k \times 10^4$ (mhos. cm^{-1})	$A/l \times 10$ (cm)
Salt : NH_4NO_3			
0.005	0.20	0.8306	2.41
0.01	0.25	1.038	2.41
0.02	0.30	1.246	2.41
0.04	0.35	1.454	2.41
0.06	0.40	1.661	2.41
0.08	0.45	1.869	2.41
Salt : $(NH_4)_2SO_4$			
0.005	0.25	1.038	2.41
0.01	0.30	1.246	2.41
0.02	0.35	1.454	2.41
0.04	0.40	1.661	2.41
0.06	0.45	1.869	2.41
0.08	0.55	2.284	2.41
Salt : $(NH_4)_3PO_4$			
0.005	0.30	1.246	2.41
0.01	0.40	1.661	2.41
0.02	0.45	1.869	2.41
0.04	0.50	2.077	2.41
0.06	0.55	2.284	2.41
0.08	0.60	2.492	2.41

Table 5 suggests that the soil membrane studied has the same value of A/l, i.e, 0.24 cm for all the solutions used. In the present study, the salt solutions are fairly dilute and the membrane constant appears to vary negligibly in the concentration range used here.

Taking viscosity for the solutions of ammonium nitrate, ammonium sulphate and ammonium phosphate as $2.87 \pm 0.01 \times 10^{-2}$ p ; $2.89 \pm 0.03^{-2} \times 10^{-2}$ p and $2.96 \pm 0.06 \times 10^{-2}$ p respectively, the average pore radii for different solutions at different

centrations and at 35° were calculated by using following expression[8] :

$$\left(\frac{J_V}{\Delta P}\right)_{\Delta\phi=0}=\frac{n\pi r^4}{8\eta l}=\frac{A}{l}\cdot\frac{r^2}{8\eta}$$

$$r=\left(\frac{8\eta(J_V/\Delta P)_{\Delta\phi=0}}{A/l}\right)^{\frac{1}{2}} \quad \ldots (10)$$

ere

η is the viscosity of the permeant,

J_V is the volume flux,

ΔP is the pressure difference in cm of the meant and

$\Delta\phi$ the electrical potential difference.

The pore radii thus calculated are given in ble 6.

TABLE 6—AVERAGE PORE RADII OF THE SOIL MEMBRANE

Concentration (mol. l^{-1})	Pore radius ($\times 10^{8}$ cm)
Salt : Ammonium nitrate	
0.005	2.62
0.01	2.35
0.02	2.26
0.04	2.14
0.06	2.07
0.08	2.02
Salt : Ammonium sulphate	
0.005	2.42
0.01	2.19
0.02	2.10
0.04	2.03
0.06	1.99
0.08	1.94
Salt : Ammonium phosphate	
0.005	2.24
0.01	2.14
0.02	2.09
0.04	2.04
0.06	2.01
0.08	1.94

Table 6 shows that the pore radius somewhat decreases with increasing concentration for all the salts studied here. This may be attributed to the change in the electrical double layer at the solution-soil interface caused by electrostatic interactions.

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Carbon, Nitrogen and Sulphur Mineralisation in a Soil from Three Decomposing Plant Materials of Varying C/N, C/S and N/S Ratios

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A laboratory incubation study was undertaken to compare the carbon, nitrogen and sulphur mineralisation in a soil from three decomposing plant materials, namely, dhaincha (*Sesbania aculeata*), cowpea (*Vigna sinensis*) and water-hyacinth (*Eichornia crasspipes*) of varying C/N, C/S and N/S ratios applied at five different levels. Both carbon and nitrogen mineralisation from three different plant materials followed the order: dhaincha>cowpea>water-hyacinth. The extent of carbon mineralisation was found to be a reflection of the organic carbon content of the added organic matter. C/N ratio of the added plant material predominantly controls nitrogen mineralisation in soil. While sulphur mineralisation was found not only to depend on the sulphur content of the added plant material but also to their composition in relation to organic carbon and total nitrogen.

ADDITION of plant residue to supplement N, P, S and other nutrient requirements of crops is usually included in the management practices of cultivated soils. Most of the nitrogen and sulphur in soil are present in organic form and plants are largely dependent upon the mineralisation of nitrogen and sulphur from the native or added organic matter in soil.

Since carbon, nitrogen and sulphur exist in close relationship in soil organic matter, many workers are of opinion that their mineralisation would be similar (Walker[1]; Bardsley and Lancaster[2]). But Hesse[3] failed to observe sulphur mineralisation in soil where appreciable amounts of carbon and nitrogen were mineralised. Barrow[4] concluded that mineralisation of added organic matter depends on its sulphur content in much the same way as the mineralisation of nitrogen depends on nitrogen content. Mukhopadhyay[5] observed that the amount of sulphur mineralised from added organic matter was closely related to the sulphur content rather than its C/S ratio. In view of the inconsistencies in the results, the present study was undertaken to investigate the relative effects of three different types of plant materials of varying C/N, C/S and N/S ratios on mineralisation of carbon, nitrogen and sulphur in soil.

Experimental

The experiment was conducted with a soil (0-15 cm layer) collected from Kalyani in Nadia district of West Bengal.

The *p*H, organic C%, total N%, CEC (mg/100 g), water holding capacity, available nitrogen (NH_4^+ NO_3' in mg/100 g) and available sulphate sulphur (0.15% $CaCl_2$ extractable in mg/100 g) contents of the soil are 8.4, 0.27, 0.03, 9.1, 31.8, 39.1 and 38.1 respectively.

The oven dried plant samples used in the present study were dhaincha (*Sesbania aculeta*) leaves, vegetative parts of cowpea (*Vigna sinensis*) and water-hyacinth (*Eichornia crasspipes*) with 36.45, 36.03 and 29.97% carbon, 3.64, 2.80 and 2.0% nitrogen and 0.431, 0.462 and 0.212% sulphur respectively.

Besides control, where no source of organic matter was added, treatments with respect to each of the above material samples were added separately @ 0.5, 1.0, 1.5, 2.0 and 2.5% of the soil.

For each of the above treatments duplicate samples of 10 g soil were taken in a series of glass tubes (size 15 cm×2.5 cm) and the requisite quantities of treatment materials were separately mixed with the soil and incubated for 6 weeks maintaining moisture levels corresponding to 50% of the moisture holding capacity of the soil. Separate sets were maintained for monitoring the changes in the mineralisation of carbon, nitrogen and sulphur. Three tubes were placed inside an Erlenmeyer flask of 1 litre capacity together with a tube containing a known concentration of NaOH solution for estimating the amount of CO_2 evolved during the incubation period. A few ml of water was placed in the flask to maintain high humidity[6]. The flask was closed and incubated at laboratory room temperature ($30\pm2°$) for 6 weeks.

Available nitrogen was determined following the method of Hesse[7] after extracting the soil with 2*M* KCl solution. Available sulphate sulphur was determined following the reduction method of Johnson and Nishita[8] after extracting the soil with 0.15% $CaCl_2$ solution (Soil : Solution ratio 1 : 2.5).

TABLE 1—EFFECT OF PLANT MATERIALS ADDITION ON MINERALISATION OF CARBON, NITROGEN AND SULPHUR IN SOIL

Level of addition	Type of plant material	Carbon		Available nitrogen		Available sulphur	
		A	B	A	B	A	B
0.5%	Cowpea	387.6	210.7	41.6	− 5.2	6.2	−51.8
	Waterhyacinth	234.0	57.1	33.8	−13.0	78.6	20.6
	Dhaincha	484.0	257.1	52.0	5.2	25.0	−33.0
1.0%	Cowpea	431.5	254.6	52.0	5.2	34.3	−23.7
	Waterhyacinth	357.3	180.4	33.8	−13.0	3.1	−54.9
	Dhaincha	466.8	289.9	96.3	49.5	28.1	−29.1
1.5%	Cowpea	520.0	343.1	52.0	5.2	160.8	110.7
	Waterhyacinth	434.8	257.9	23.4	−23.4	3.1	−54.9
	Dhaincha	368.4	391.5	78.0	31.2	43.7	−14.3
2.0%	Cowpea	416.7	239.8	67.2	20.4	195 3	137.3
	Waterhyacinth	439.7	262.8	20.8	−26.0	15.5	−42.5
	Dhaincha	453.0	276.3	64.6	17.8	6.2	−51.8
2.5%	Cowpea	606.0	429.1	75.5	28.7	217.5	159.5
	Waterhyacinth	469.0	292.1	33.8	−13.0	21.9	−36.1
	Dhaincha	606.0	429.1	56.0	9.2	6.2	−51.8

A = Available S/Available N/C mineralised in mg/100 g of soil.
B = Increase over control in mg/100 g soil.

In calculating the overall effect of added organic materials in the soil, the results of analysis of the soil not treated with organic matter were subtracted from those of soil plus organic matter.

Results and Discussion

Irrespective of the nature of the added plant materials, carbon mineralisation increased with the increase in their amounts (Table 1). But the rate of CO_2 evolution followed the order : dhaincha > cowpea ≫ water-hyacinth, which is also the order of their initial carbon contents. In order to have a closer look at the increases of CO_2 production the increments for each 0.5% (w/w) in different ranges of addition were computed. The increment was higher in the 0-0.5% range than in the other ranges computed (Table 2) in the case of dhaincha and cowpea. But in the case of water-hyacinth the increase was maximum in the range of 0.5 to 1.0%. No explanations are forthcoming at this stage of investigation.

TABLE 2—THE RELATIONSHIP OF ADDED INCREMENTS OF DIFFERENT LEVELS OF PLANT MATERIALS TO INCREASE IN THE PRODUCTION OF CO_2 AND AVAILABLE N AND S IN THE SOIL

Nature of added plant material		Mineralisation of C, N and S (mg/100 g) per 0 5% increase in the level of plant material addition				
		0-0.5%	0.5-1.0%	1.0-1.5%	1.5-2.0%	2.0-2.5%
Cowpea	C	210.7	43 9	88.5	—	—
	N	− 5.2	10.4	0	15.2	8.3
	S	−51.8	28.1	134.4	26.6	22.2
Dhaincha	C	257.1	32.8	102.0	—	—
	N	5.2	44.3	−18.3	−13.4	−8.6
	S	−33.0	3.9	14.8	−37.5	0
Water-hyacinth	C	57.1	123.3	77.5	4.9	29.3
	N	−13.0	0	−10.4	−12.6	13.0
	S	—	—	0	12.4	6.4

Although the highest value of available nitrogen (2 *M* KCl extractable $NH_4^+ + NO_3'$) was observed in the dhaincha treatment (96.3 mg/100 g at 1% level of addition) and the least in the water-hyacinth treatment (33.8 mg/100 g at 1% level), the difference in the amount of available nitrogen between the treated soil and untreated control tends to rise upto 2.5% level in the cowpea added soil (28.7 mg/100 g) but upto 1% level in the dhaincha treated soil (49.5 mg/100 g) (Table 1), whereas, immobilisation of available nitrogen was noted in the water-hyacinth treated soil. However, possibility of some amount of denitrification loss from the soil cannot be excluded. The quantity of nitrogen mineralised from the added organic matter in soil during decomposition obviously is mainly a function of the chemical nature and amount of organic matter and the degree of microbial activity. The results shown in Table 2 support this contention. Since nitrogen mineralisation is largely influenced by C/N ratio of the added organic matter it is pertinent to view the results in terms of this ratio. Thus C/N ratio of dhaincha sample was the least (10.0) and that of water-hyacinth the highest (14.9), cowpea being intermediate between the two (12.8). The order of reactivity is also in this order.

Analysis of 0.15% $CaCl_2$ extractable sulphate sulphur shows a trend similar to nitrogen. Available sulphate sulphur content of the soil increased with increasing amount of cowpea addition, i.e., from 6.2 mg/100 g at 5% level to 217.5 mg/100 g at the 2.5% level of addition, the maximum increase being observed (Table 2) between 1 and 1.5% level (34.3 to 160.8 mg/100 g). But in dhaincha treated soil a similar trend was expressed only upto 1.5% level of addition. In the water-hyacinth treatment, the highest value of available sulphate sulphur was observed at the 0.5% level of addition (78.6 mg/100 g) which sharply decreased to 3.1 mg/100 g at 1% and 1.5% level of addition.

Sulphur mineralisation, it appeared, was not only dependent on the sulphur content of the added plant material but also on C/S and N/S ratios. Similar conclusions were reported by Barrow[8].

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Heterocyclic Compounds : Sulphur as a Potential Oxidant : Preparation of 5-Alkyl/arylimino-2,4-dialkyl/aryl-3-thio/oxo-1,2,4-thiadiazolidines

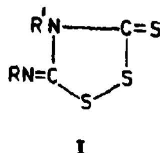
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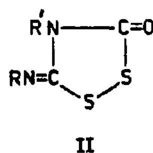
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Some interesting observations involving reaction of excess of benzylamine and isoperthiocyanic acid (Ia), the so-called isothiocyanate sulphides (Ib-If) and isothiocyanate oxides (II) have been reported. In these reactions 5-alkyl/arylimino-2,4-dialkyl/aryl-3-thio-1,2,4-thiadiazolidines (III) and 5-arylimino-2,4-dialkyl/aryl-3-oxo-1,2,4-thiadiazolidines (VI) have been isolated. In all these reactions, elemental sulphur initially formed acts as a potential oxidant in the oxidative cyclisation of intermediates, viz., 2,4-dithiobiurets (IV) and 2-thiobiurets (VII).

INTERACTION of 5-imino-3-thio-1,2,4-dithiazolidine called isoperthiocyanic acid (Ia) and compounds related to this, i.e., 4-substituted-5-substituted imino-3-thio-1,2,4-dithiazolidines (Ib-If) and 3-oxo-4-substituted-5-substituted imino-1,2,4-dithiazolidines (II) also called isothiocyanate sulphides and oxides, respectively, with aryl and alkyl amines has been investigated earlier[1-4]. We have now noticed that interaction of excess of benzylamine with I and II gives the related 1,2,4-thiadiazolidines, 2,4-dithiobiurets and 2-thiobiurets, depending upon the reaction conditions, viz., boiling benzylamine or boiling ethanol media. All these have been prepared for the first time. The present communication is a record of these investigations.



I

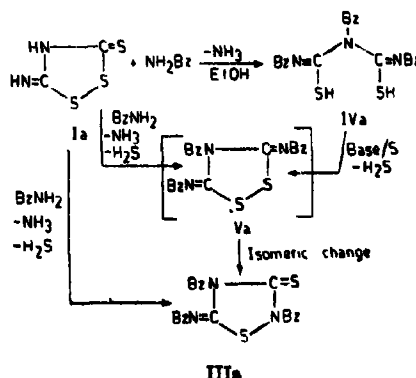


II

When the interaction of Ia has been carried out in boiling benzylamine for 3 hr, evolution of hydrogen sulphide is quite perceptible. On treatment with aqueous hydrochloric acid, a product, crystallized from ethanol, m.p. 146° is isolated. The product is found non-desulphurisable when boiled with alkaline plumbite solution. It did not react with phenyl isothiocyanate, nor with carbon disulphide indicating the absence of a free imino group. The ir spectrum of the product clearly showed νC=S (1200 cm^{-1}), νC=N (1580 cm^{-1}) and νC–S (705 cm^{-1})[7,8] bands. A band due to νS–S, however, is missing. On the basis of all these facts, the product is assigned the structure 5-benzylimino-2,4-dibenzyl-3-thio-1,2,4-thiadiazolidine (IIIa).

When the interaction of Ia has been carried out with benzylamine in boiling ethanolic medium, elemental sulphur is left as residue on cooling and filtering. The alcoholic filtrate on treatment with dilute hydrochloric acid gives a product, crystallized from ethanol, m.p. 140°. This product is found desulphurisable when boiled with alkaline plumbite solution. On boiling with benzylamine, in presence of elemental sulphur, it is oxidatively cyclized into IIIa with evolution of hydrogen sulphide. Therefore, it is expected to be 1,3,5-tribenzyl-2,4-dithiobiuret (IVa).

Formation of IIIa from the direct reaction of Ia and benzylamine and formation of IVa on reaction of Ia and benzylamine in ethanolic medium and conversion of IVa into IIIa has demonstrated the exact path of the reaction in which elemental sulphur acts as an oxidant for IVa. The mechanism may be stated as follows :



IIIa

The formation of IIIa will essentially take place through an intermediate 1,2,4-dithiazolidine Va[8] (not isolated) which is not likely to survive in basic conditions and therefore will be rearranged into IIIa.

When the interaction of benzylamine and Ib has been carried out without any solvent, hydrogen

sulphide is found eliminated and the product, m.p. 145° has been isolated. It is assigned the structure 2-benzyl-4-phenyl-5-phenylimino-3-thio-1,2,4-thiadiazolidine (IIIb) on the basis of the following facts :

The product is found non-desulphurisable when boiled with alkaline plumbite solution. The ir spectrum of the product clearly showed the presence of νC=S (1200 cm^{-1}), νC=N (1580 cm^{-1}) and νC–S (705 cm^{-1})[7,8] bands.

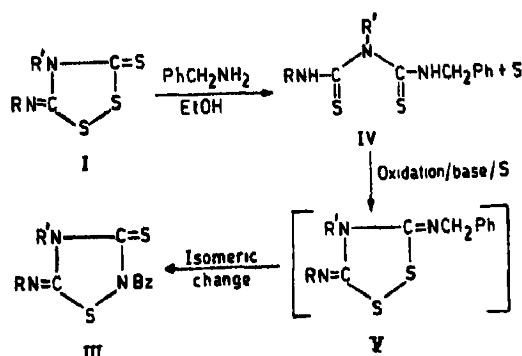
When the reaction of benzylamine is extended to other isothiocyanate sulphides (Ic-If), the related products IIIc-IIIf have been isolated.

Ib on reaction with benzylamine in boiling ethanolic medium did not give 5-benzyl-1,3-diaryl-2,4-dithiobiurets. In most of the cases, unreacted product is isolated while in the case of reaction with Ib, small quantity of 3-benzyl-1-phenyl thiocarbamide, m.p. 149° along with elemental sulphur is detected.

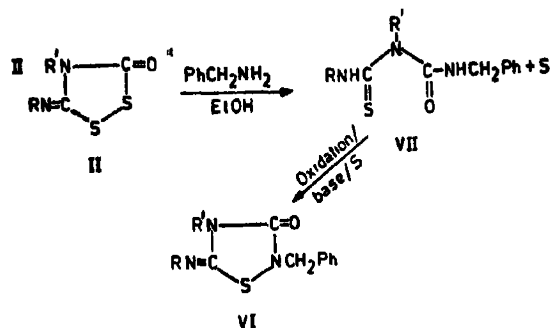
The reaction of benzylamine with IIa has also been carried out both in boiling benzylamine medium and boiling ethanolic medium. In the former, hydrogen sulphide is eliminated and a solid, m.p. 134° has been isolated. This has been assigned structure 2-benzyl-3-oxo-4-phenyl-5-phenylimino-1,2,4-thiadiazolidine (VIa) on the basis of the following facts :

The product is non-desulphurisable when boiled with alkaline plumbite solution. The ir spectrum of the product clearly indicated the presence of νC=O (1620 cm^{-1}), νC=N (1580 cm^{-1}) and νC=S (705 cm^{-1}) bands.

The reaction of Ia and benzylamine in boiling ethanolic medium forms a product, crystallized from ethanol, m.p. 138° along with elemental sulphur. The product is identified through m.m.p. as 5-benzyl-1, 3-diphenyl-2, thiobiuret (VIIa)[9]. VIIa is oxidized to VIa on boiling with benzylamine in presence of elemental sulphur. On reaction with benzylamine, IIb and IIc give VIb and VIc respectively. All these reactions may be represented as follows :



where (a) R=R'=Hydrogen (in I only) and R=R'=Benzyl
(b) R=R'=Phenyl
(c) R=Phenyl, R'=p-Tolyl
(d) R=Phenyl, R'=m-Tolyl
(e) R=Phenyl, R'=p-Chlorophenyl
(f) R=Phenyl, R'=m-Chlorophenyl



where R=R'=(a) Phenyl, (b) p-Tolyl, (c) Methyl (in II only) and benzyl (in VI only)

Experimental

The required isoperthiocyanic acid[10], isothiocyanate sulphides[11] and isothiocyanate oxides[12] were prepared according to procedures described earlier.

(1) *Interaction of isoperthiocyanic acid (Ia) and benzylamine :*

(a) *Reaction without solvent :* When to isoperthiocyanic acid (2 g) is added benzylamine (10 ml), it gradually dissolves with liberation of heat. It is then refluxed for 3 hr when hydrogen sulphide is evolved. The reaction mixture is cooled to 0° and slowly acidified with dilute hydrochloric acid (4 *N*) without allowing the temperature to rise above 10°. A sticky solid is obtained which is triturated several times with petroleum ether when a white solid (IIIa) is obtained. It is crystallized from ethanol, m.p. 146° (Found : N, 10.45 ; S, 15.05. $C_{22}H_{21}N_3S_2$ requires N, 10.42 ; S, 15.99%).

(b) *Reaction in ethanolic medium:* Isoperthiocyanic acid (2 g) is suspended in 20 ml ethanol and 10 ml benzylamine is added. It is then refluxed for 1 hr. The evolution of hydrogen sulphide and ammonia are clearly perceptible. After 1 hr the reaction mixture is cooled. The elemental sulphur that separates out is filtered off, and the filtrate is acidified with dilute hydrochloric acid (4 *N*) with cooling when a white sticky mass, solidified on trituration with petroleum ether followed by ethanol, is obtained. It is crystallized from ethanol, m.p. 140° (Found : N, 9.88 ; S, 15.93. $C_{23}H_{23}N_3S_2$ requires N, 10.37 ; S, 15.81%).

(2) *Interaction of isothiocyanate sulphides (Ib-If) and benzylamine :* Details of a typical experiment (where R=R'=phenyl) are as follows :

To 2 g of isothiocyanate sulphide is added 10 ml of benzylamine. The solution warmed up as soon as benzylamine is added. It is then refluxed for 3 hr when evolution of hydrogen sulphide is noticed. After 3 hr, the reaction mixture is worked up as usual when a solid, crystallized from ethanol, m.p. 145° is obtained (Found : N, 11.80 ; S, 17.20, $C_{21}H_{17}N_3S_2$ requires N, 11.20 ; S, 17.07%).

TABLE 1—4-ARYL-2-BENZYL-5-PHENYLIMINO-3-THIO-1,2,4-THIADIAZOLIDINE(III) AND 4-ARYL-5-ARYLIMINO-2-BENZYL-3-OXO-1,2,4-THIADIAZOLIDINE(VI)

Reactants for III : I, 2 g and benzylamine 10 ml.
Reactants for VI : II, 2 g and benzylamine 10 ml.

Sl. No.	1,2,4-dithiazolidine	1,2,4-thiadiazolidine (g) m.p. °C	Analysis Found	Analysis Required
1.	4-Phenyl-5-phenylimino-3-thio-(Ib)	2-Benzyl-4-phenyl-5-phenylimino-3-thio-(IIIb)(2) 145°	N, 11.86 S, 17.20	11.20 17.07
2.	5-Phenylimino-4-p-tolyl-3-thio-(Ic)	2-Benzyl-5-phenylimino-4-p-tolyl-3-thio-(IIIc)(1.8) 140°	N, 10.47 S 15.96	10.80 16.45
3.	5-Phenylimino-4-m-tolyl-3-thio-(Id)	2-Benzyl-5-phenylimino-4-m-tolyl-3-thio-(IIId)(1.5) 143°	N, 11.14 S, 16.08	10.80 16.45
4.	4-p-Chlorophenyl-5-phenylimino-3-thio-(Ie)	2-Benzyl-4-p-chlorophenyl-5-phenylimino-3-thio-(IIIe)(2) 147°	N, 10.44 S, 15.89	10.26 15.62
5.	4-m-Chlorophenyl-5-phenylimino-3-thio-(If)	2-Benzyl-4-m-chlorophenyl-5-phenylimino-3-thio-(IIIf)(1.8) 142°	N, 9.98 S, 15.77	10.26 15.62
6.	3-Oxo-4-phenyl-5-phenylimino-(IIa)	2-Benzyl-3-oxo-4-phenyl-5-phenylimino-(VIa)(2) 134°	N, 11.29 S, 9.41	11.69 8.91
7.	3-Oxo-4-p-tolyl-5-p-tolylimino-(IIb)	2-Benzyl-3-oxo-4-p-tolyl-5-p-tolylimino-(VIb)(2) 125°	N, 10 57 S, 7 88	10.85 8.26
8.	4-Methyl-5-methylimino-3-oxo-(IIc)	5-Benzylimino-2,4-dibenzyl-3-oxo-(VIc)(1 6) 136°	N, 11.88 S, 9.19	11.60 8.91

The reaction of benzylamine has been extended to other 4-aryl-5-phenylimino-3-thio-1, 2, 4-dithiazolidines (Ib-If), and the corresponding 1,2,4-thiadiazolidines (IIIb-IIIf) have been isolated in excellent yields. These are listed in Table 1.

(3) *Interaction of isothiocyanate oxides (IIa-IIc) and benzylamine :* Details of a typical experiment (where, R=R′=phenyl) are as follows :

(a) *Reaction without solvent :* To IIa (2 g) is added 10 ml of benzylamine. It is then refluxed for 3 hr when hydrogen sulphide is found eliminated. After 3 hr, the reaction mixture is worked up as usual when a white solid, crystallized from ethanol, m.p. 134° (VIa) is obtained. (Found : N, 11,29 ; S, 9.41. $C_{21}H_{17}N_3SO$ requires N, 11.69 ; S, 8.91%).

The reaction of benzylamine when extended to IIb and IIc, the corresponding products VIb and VIc have been obtained. These have been listed in Table 1.

(*b*) *Reaction in ethanolic medium :* 2 g of isothiocyanate oxide is suspended in 20 ml of ethanol and 1 ml of benzylamine is added. It is refluxed for 3 hr when no hydrogen sulphide is noticed from the reaction[8]. After 3 hr the elemental sulphur that separated out is filtered and the filtrate acidified with dilute hydrochloric acid (4 *N*) when a white solid, crystallized from ethanol, m. p. 138° (VIIa) is obtained. (Found : N, 10.62; S, 15.88. $C_{21}H_{19}N_3SO$ requires N, 10.71 ; S, 16.34%).

On refluxing with elemental sulphur and benzylamine for 2 hr VIIa is oxidatively cyclised into VIa with evolution of hydrogen sulphide.

The reaction of benzylamine is also extended to IIb and IIc and the corresponding compounds VIIb and VIIc (where R=R′=benzyl) have been isolated. The formation of latter will occur by the replacement of methyl groups in IIc with a bulky benzyl group.

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Oxidative Decarboxylation : Partial Synthesis of Aegiceradienol† (*nor* Echinocystadienol)

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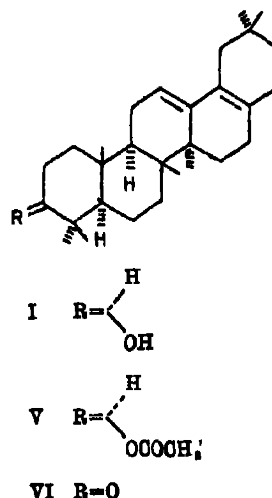
3β-Acetoxy olean-12-en-28-oic acid (III) (acetyl oleanolic acid) on oxidative decarboxylation with lead tetraacetate-cupric acetate gave a complex diene mixture (IV) which isomerised on heating with acetic acid-hydrochloric acid to 28-*nor* olean-12,17-dien-3 β-yl acetate (V) (aegiceradienyl acetate). Hydrolysis of the acetate gave 28-*nor* olean-12,17-dien-3β-ol(I) (aegiceradienol). 3-Oxo olean-12-en-28-oic acid (oleanonic acid) (VII) on oxidative decarboxylation gave 28-*nor* olean-12,17-dien-3-one (VI) which on reduction with sodium borohydride gave 28-*nor* olean-12,17-dien 3β-ol (aegiceradienol).

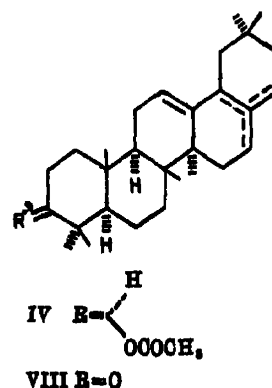
RAO and Bose[1] isolated the first 28-*nor* olean triterpene alcohol, 28-*nor* olean-12,17-dien-3β-ol, aegiceradienol *nor* echinocystadienol (I) from the bark of *Aegiceras majus* Gaertn. (Syn, *A. Corniculatum* Blanco) besides isorhamnetin and genin-A. Barton and Crook[2] prepared *nor* echinocystadienol (I) by the pyrolysis of isodehydrooleanolic acid. Noller and Carson[3] prepared *nor* echinocystadienol (I) by vaccum distillation of echinocystic acid. Hansen and Lewis[4] remarked that aegiceradienol (I) may be an artefact derived from genin-A.

Lead tetraacetate is a versatile reagent and is known to cause oxidative decarboxylation[5,6,7]. Khastgir *et al*[8] in connection with the work on baccatin a nor-triterpene peroxide from *Sapium baccatum* Roxb. subjected crategolic acid diacetate (2α, 3β-diacetoxy olean 12-en-28-oic acid) to oxidative decarboxylation using lead tetraacetate and obtained 2α, 3β-diacetoxy 28-*nor* olean-12,17-dien. Bacha and Kochi[9] found that cupric acetate had marked catalytic effect on the oxidative decarboxylation of primary and secondary acids by lead tetraacetate. In the present investigation oleanolic acid isolated in our laboratory from the roots of *Lantana camara* Linn[10] is subjected to cupric acetate catalysed lead tetraacetate decarboxylation to aegiceradienol.

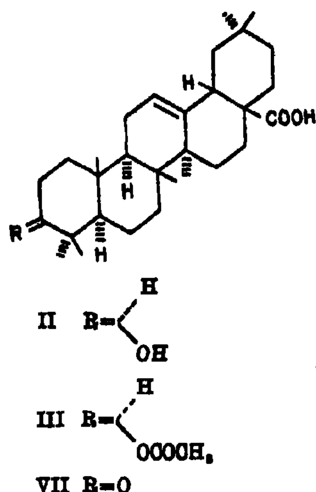
Acetyl oleanolic acid (III), on heating with lead tetraacetate-cupric acetate in dry benzene-pyridine gave an inseparable complex diene mixture (IV) which on heating with acetic acid-hydrochloric acid gave a single compound. It's physical characteristics closely resembled aegiceradienyl acetate (V) m.p. 185-187° ; $[\alpha]_D^{30}+64°$ (c, 0.81 in $CHCl_3$) : lit[1] m.p. 187-188 ; $[\alpha]_D+62$: λ max 237 and 244 nm. Hydrolysis of the acetate (V) gave the alcohol whose physical characteristics were in agreement with aegiceradienol (I) m.p. 188-190° ; $[\alpha]_D^{30}+76$ (c, 0.78 in $CHCl_3$) : lit[1] m.p. 189-191° ; $[\alpha]_D+79°$. No carboxylic carbonyl absorption in the ir spectrum. Cromium trioxide-pyridine oxidation of the alcohol (I) gave the dienone identical in all respects with 28-*nor* olean-12,17-dien-3-one (VI) m.p. 120-122° ; $[\alpha]_D^{30}+114°$ (c, 0.82 in $CHCl_3$) : lit[1] m.p. 121-123° ; $[\alpha]_D+114°$.

The above findings are substantiated by subjecting oleanonic acid (VII) to oxidative decarboxylation which also gave a complex diene mixture (VIII),





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isomerisation of which with acetic acid-hydrochloric acid gave a dienone identical with the dienone (VI) obtained above. Reduction of the dienone (VI) with sodium borohydride gave the dienol identical in all respects with the dienol (I) obtained above by the hydrolysis of dienyl acetate (V).

Direct comparison with authentic sample could not be made as it could not be secured.

Experimental

The melting points are uncorrected, ir spectra were recorded on Perkin-Elmer 237 spectrophotometer.

Action of lead tetraacetate-cupric acetate on acetyle oleanolic acid (III) : Complex diene mixture (IV) : Acetyl oleanolic acid (3.5 g) was dissolved in dry benzene-pyridine mixture (4 : 1 ; 75 ml), lead tetraacetate (10 g) and cupric acetate (1 g) were added and gently warmed till the evolution of carbon dioxide commenced. At this point the source of heat was removed and reapplied and refluxed for 2 hr after the evolution of carbon dioxide had ceased. The reaction mixture was cooled, diluted with ether (100 ml) filtered and the residue washed with ether (3×100 ml). The combined ether solution (400 ml) was washed with cold sodium hydroxide (10% ; 3×100 ml) and hydrochloric acid (2*N* ; 3×50 ml). The dried ether solution gave a colourless semisolid (2 g) on removal of the solvent. It was found to be a complex diene mixture (tlc).

Isomerisation of the complex diene mixture (IV) ; Aegiceradienyl acetate (V) : The complex diene mixture (2 g) in glacial acetic acid-conc hydrochloric acid mixture (5 : 1 ; 60 ml) was heated for 6 hr on water bath and diluted with water when a pale brown solid separated (1.6 g). It was chromatographed on a column of neutral alumina. Elution with benzene-pet. ether (1 : 1) gave a colourless solid (1.4 g) homogeneous on tlc. It crystallized from methanol-chloroform as colourless needles, m.p. 185-187° ; $[\alpha]_D^{30°}+64°$ (c, 0.81 $CHCl_3$) : lit[1] m.p. 187-188 ; $[\alpha]_D+62°$, λ_{max}^{EtOH} 237 and 244 nm (log ε 4.25 and 4.18 respectively), ν_{max} at 1725, 1760, 1240 cm^{-1} (Found : C, 82.24 ; H, 10.58. $C_{31}H_{48}O_2$ requires C, 82.27 ; H, 10.65%).

Hydrolysis of aegiceradienyl acetate (V) ; Aegiceradienol(I) : The acetate (1 g) was refluxed with methanolic potassium hydroxide (10% ; 50 ml) for 1 hr. The solvent was removed and the product isolated by extraction with ether. The dried ether extract on removal of the solvent gave a pale yellow solid (0.800 g) crystallized from ethanol as colourless needles, m. p. 188-190° ; $[\alpha]_D^{30°}+76$ (c 0.78 in $CHCl_3$) ; lit[1] m. p. 189-191° ; $[\alpha]_D+79$, ν_{max} (Nujol) 3630 cm^{-1} (OH) no carboxylic (C=O) band (Found : C, 84.62, H, 11.2. $C_{29}H_{46}O$ requires C, 84.80 and 11.3%).

Chromium trioxide-pyridine oxidation of aegiceradienol (I) ; 28-nor olean-12,17-dien-3-one (VI) : A solution of the dienol (500 mg) in pyridine (25 ml) was treated with chromium trioxide (200 mg) and left at room temperature for 24 hr. It was then diluted with hydrochloric acid (1% ; 50 ml) and extracted with ether. The ether extract was washed with dilute hydrochloric acid, water, dried and evaporated to yield a pale yellow solid. It crystallized from methanol as colourless needles m. p. 120-122° ; $[\alpha]_D^{30°}+114°$ (c, 0.82 in $CHCl_3$) : lit[1] m. p. 121-123° ; $[\alpha]_D+114°$, ν_{max} (Nujol) 1704 cm^{-1} (C=O). (Found : C, 85.23 ; H, 10.78. $C_{29}H_{44}O$ requires C, 85.29 ; H, 10.78%).

Action of lead tetraacetate-cupric acetate on oleanonic acid (VII) ; complex diene mixture (VIII) : To a solution of oleanonic acid (2 g) in dry benzene-pyridine (4 : 1 ; 75 ml), lead tetraacetate (10 g) and cupric acetate (1 g) were added and gently warmed until the evolution of carbon dioxide commenced. At this point the source of heat was removed and reapplied after the evolution of carbon dioxide had ceased. The reaction mixture was then refluxed for 2 hr and worked out as above. The reaction product (1.5 g) was found to be a complex diene mixture (tlc).

Acetic acid-hydrochloric acid isomerisation of the above complex mixture (VIII) : 28-nor olean-12,17-dien-3-one(VI) : The diene mixture (1.5 g) was heated on a water bath for 6 hr with glacial acetic acid-concentrated hydrochloric acid (5 : 1 ; 60 ml) and worked out as above. The product (1.2 g) was identical with 28-*nor* olean-12,17-dien-3 one (VI) obtained above by chromium trioxide oxidation of aegiceradienol.

Reduction of 28-nor olean-12,17-dien-3-one (VI) ; Aegiceradienol (I) : To a solution of the dienone (500 mg) in methanol (50 ml), sodium borohydride (500 mg) was added in small quantities for a period of 30 min and left for 2 hr. It was acidified with hydrochloric acid and extracted with ether. The ether extract was washed with water, dried and the solvent removed to yield aegiceradienol (400 mg), identical with aegiceradienol obtained above by isomerisation of the diene mixture (IV) followed by hydrolysis.

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Synthesis of 3-Hydroxy-2-(3′-pyridyl) Chromones and -2-(3′-pyridyl)-Chromones

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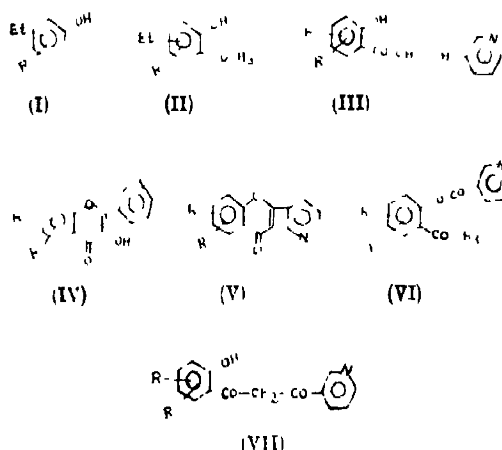
A few ethyl phenols and their corresponding 2′-hydroxy-acetophenones were synthesised from respective o-hydroxy-acetophenones and a few 3-hydroxy-2-(3′-pyridyl)chromones and 2-(3′-pyridyl) chromones were synthesised from o-hydroxy-acetophenones. The compounds were tested for their physiological activities.

ACRYLOPHENONES having a heterocyclic substituent at 3 positions are active against *M tuberculosis* and *S. aureus*[1-9]. 2-Phenyl and 2-methyl chromones are reported to possess pharmacological activity[10-15]. 6-Chloro-2-(2′-quinolyl) chromones are found to be active against sarcoma-180[16] Taking into account these activities of acrylophenones and chromones having a heterocyclic substitutent, a number of such compounds have been synthesised and results are reported in this paper

Some new ethylphenols (I), used as starting materials, were prepared from substituted acetophenones by Clemmenson's reduction method The various substituted acetophenones such as methyl-ethyl-halogeno-ethyl-2′,4′-,5′-dichloro,-2′,4′-dibromo and -3′, 4′-benzo-2′-hydroxy acetophenones (II) were prepared from the corresponding acetates by Fries reaction (Table 1). These acetophenones (II), on condensation with pyridine-3-aldehyde in basic medium yielded the corresponding 3-(3′-pyridyl)-acrylophenones (III) The acrylophenones (III) on treatment with alkaline hydrogen peroxide under Alger-Flynn-Oyamada reaction condition afforded the corresponding 3-hydroxy-2-(3-pyridyl) chromones (IV). The acrylophenones (III) were subjected to oxidative ring closure by selenium dioxide to give the corresponding 2-(3′-pyridyl) chromones (V) The same 2-(3′-pyridyl) chromones (V) were also obtained by an alternative route. The acetophenones (II) were esterified by nicotinyl chloride in dry pyridine. The resulting esters (VI) were converted into 1, 3-propanediones (VII) by Baker-Venkataraman transformation. 1, 3-Propanediones (VII) on cyclodehydration under acidic condition yielded the same 2-(3′-pyridyl) chromones (V) as were obtained by SeO_2 method. The identify was proved by mixed melting points which showed no depression.

Infrared spectra : The infrared spectra of a few compounds were scanned in nujol mull. (3′-Pyridyl)-2′-hydroxy-acrylophenones showed strong absorption bands in the region 1650-1700 cm^{-1} (C=O) and 1610-1620 cm^{-1}(C=C). The ir spectra of 2-(3′-pyridyl) chromones showed bands in the range of 1630-1690 cm^{-1} and 1560-1600 cm^{-1}, characteristic of chromone carbonyl and ethylinic double bond respectively

Physiological activity Some ethyl phenols (I) methyl substituted 2′-hydroxy acrylophenones (II), 3-hydroxy-2-(3′-pyridyl) chromones (IV) and 2-(3′-pyridyl) chromones (V) have been tested for their physiological activity 2-Ethyl-5-chlorophenol was found to be toxic Some acrylophenones (III) have been tested for anti-trichnella spiralis, antiviral, antithrilis, gastric secretion, pylorus ligation etc., but none of them was found to be active 3-Hydroxy-2-(3′-pyridyl) chromones (IV) and 2-(3′-pyridyl) chromones (V) have been tested for gastric secretion, pylorus ligation and anthalmentic activities. Only 2-(3′-pyridyl)-6-8-dichloro chromones have shown anthelmentic activity.



Experimental

(1) *Ethyl substituted phenols (I)* A mixture of amalgamated zinc (80 g), hydrochloric acid (2 . 3 v/v , 300 ml) and alcoholic solution of 2′-hydroxy acetophenone (20 g), was refluxed for 54 hr. Concentrated hydrochloric acid was added in small

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TABLE 1—PHYSICAL DATA OF ETHYL PHENOLS (I), CORRESPONDING PHENYL ACETATES AND 2'-HYDROXY-ACETOPHENONES (II), ACRYLOPHENONES (III), 3-HYDROXY-2-(3'-PYRIDYL) CHROMONES (IV), 2-(3'-PYRIDYL) CHROMONES (V); 2-(3'-PYRIDILOXY) ACETOPHENONES (VI) AND 1 : 3 PROPANE DIONES-(VII)

Phenols Used	m.p.(b p) °C	Yield %	Corresponding Compounds: Phenyl Acetate b.p °C	Phenyl Acetate Yield %	2'-Hydroxy-acetophenone (II) m.p.(b.p.) °C	2'-Hydroxy-acetophenone (II) Yield %
6-ethyl-3-methyl	(218)	40	228	40	(270)	30
6-ethyl-4-methyl	(210)	50	232	60	(260)	40
3-chloro-6-ethyl	49	30	244	50	(258)	40
4-chloro-6-ethyl	(241)	50	227	70	(265)	50
4-bromo-6-ethyl	(163/10 mm.)	50	248	60	42	40

2'-Hydroxy-acetophenones Used	Corresponding Compounds: Compound III m.p. °C	Compound III Yield %	Compound IV m.p °C	Compound IV Yield %	Compound V m p. °C	Compound V Yield %	Compound VI m.p. °C	Compound VI Yield %	Compound VII m p. °C	Compound VII Yield %
3',5'-dibromo	210[g]	90	288[e]	40	230[L]	40	161[e]	50	158[d]	60
3',5'-dichloro	185[f]	80	262[c]	50	223[L]	50	112[f]	40	98[e]	40
3',6'-dichloro	174[g]	60	115[e]	40	191[L]	30	125[d]	50	136[d]	30
3',4'-benzo	108[j]	80	267[d]	50	218[L]	60	74[g]	60	160[d]	20
3'-ethyl-5'-chloro	160[k]	80	39[e]	80	172[L]	30	82[h]	70	168[e]	50
3'-ethyl-6'-chloro	125[f]	50	58[d]	60	47[L]	20	41[c]	20	126[b]	30
3'-ethyl-5'-bromo	94[h]	50	43[e]	25	68[L]	40	32[c]	20	138[b]	50
3'-ethyl-5'-methyl	38[i]	40	85[d]	20	102[L]	30	35[a]	40	167[c]	35
3'-ethyl-6'-methyl	41[h]	50	67[c]	30	123[L]	20	38[b]	30	140[d]	20

a = 20% acetic acid
b = 25% acetic acid
c = 30% acetic acid
d = 40% acetic acid
e = 50% acetic acid
f = 60% acetic acid
g = 70% acetic acid
h = 50% ethyl alcohol
i = 70% ethyl alcohol
j = 80% ethyl alcohol
k = 90% ethyl alcohol
L = dioxane

The elemental analysis of above compounds for C and H gave satisfactory results.

quantities (20 ml) at intervals. The thick oily layer was worked up as usual and purified by distillation.

(2) *Substituted-2'-hydroxy acetophenones (II)* · A mixture of phenol (10 g), acetic anhydride (36 ml) and fused sodium acetate (8 g) was refluxed for 2 hr. The cold reaction mixture was poured on ice-water and phenyl acetate was isolated as usual. The phenyl acetate (10 g) so obtained was treated with powdered anhydrous aluminium chloride and was heated on an oil bath for 2 hr. 2-Hydroxy acetophenones formed were isolated by steam distillation.

(3) *3-(3'-Pyridyl) acrylophenones (III) :* A 50% solution of potassium hydroxide (5 ml) was added dropwise to a cold solution of pyridine-3-aldehyde (0.3 mole) and 2'-hydroxy acetophenone (0.2 mole) in ethanol (30 ml). The reaction mixture was stirred for 4 hr and poured over crushed ice containing enough acetic acid. The resulting solid was filtered, washed with water, 5% $NaHCO_3$ solution and again with water. These compounds were crystallised from proper solvents.

(4) *3-Hydroxy-2-(3'-pyridyl) chromone (IV) :* To a cold solution of acrylophenones (0.0014 mole) in methanol (15 ml) was added a 16% solution of sodium hydroxide (2 ml) followed by dropwise addition of H_2O_2 (15% ; 2 ml). The reaction mixture was kept in an ice-chest overnight and the alkaline filtrate was acidified with acetic acid. The precipitated solid was then filtered, washed with water and crystallised from a proper solvent.

(5) *2-(3'-Pyridyl) chromones (V) :* A mixture of acrylophenone (0.003 mole), selenium dioxide (1 g) and amyl alcohol (15 ml) was refluxed for 10 hr. The hot solution was filtered and amyl alcohol was removed by steam distillation. The solids, 2-(3'-pyridyl) chromones, were crystallised from proper solvents.

(6) *1-3-Propanediones (VII) :* To an ice-cold solution of 2'-hydroxy acetophenones (II) (0.035 mole) in dry pyridine (10 ml), nicotinyl chloride (0.04 mole) was added dropwise with stirring. The reaction mixture was further stirred for 7 hr at room temperature and then poured over crushed ice containing acetic acid. The resulting esters (VI), were crystallised from proper solvents. A cold mixture of the above ester (VI) (0.45 mole), dry pyridine (15 ml), powdered potassium hydroxide (2 g) was stirred for 6 hr. The reaction mixture was poured over crushed ice containing acetic acid. The resulting solid was filtered, washed with water and crystallised from a proper solvent.

(7) *2-(3'-Pyridyl) chromones (V) from 1,3-propanediones (VII)* · A mixture of conc. sulphuric acid (10 ml), 1,3-propanedione (0.04 mole) and chloroform (40 ml) was stirred for 20 min. The reaction mixture was poured over ice-water and then made alkaline by cold sodium hydroxide solution. The chloroform layer was evaporated and the resulting solid was crystallised from a proper solvent.

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Synthesis and Reduction of Nitrones of Vanillin

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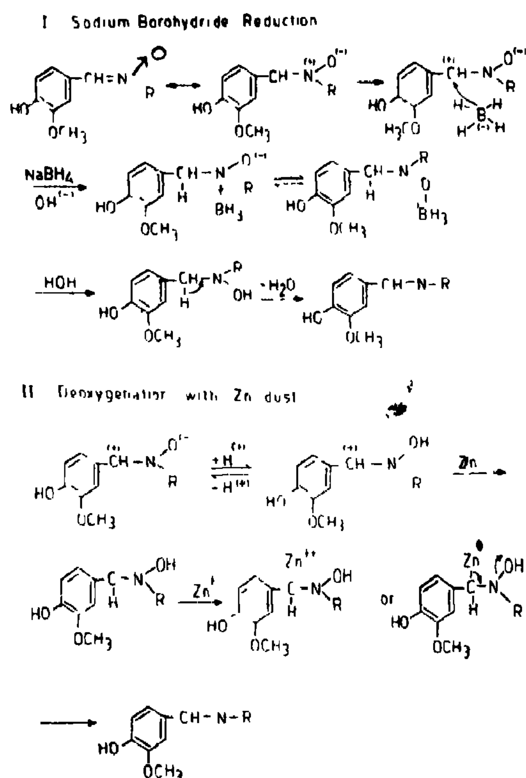
Four new vanillin nitrones have been synthesized by condensing vanillin with various arylhydroxylamines. Reduction with sodium borohydride and deoxygenation with zinc dust and acetic acid were studied

SYNTHESIS of nitrones of cinnamaldehyde was reported in an earlier communication[1]. This communication deals with the synthesis and reduction reactions of nitrones of vanillin.

These nitrones have been synthesized by condensing vanillin with phenyl hydroxylamine, *p*-tolyl and *p*-chlorophenyl hydroxylamine and *p*-naphthyl hydroxylamine. The nitrones (Table 1) have been identified and confirmed by elemental analysis and spectral studies.

UV spectra of these nitrones indicate two maxima viz., 235 and 330 nm. IR spectra give bands at 1610 cm^{-1} ($\rangle C=N-$) and 1280-60 cm^{-1} ($N\longrightarrow O$). In the nmr spectra, aromatic protons along with vinyl proton appears as a multiplet at 2.8τ, methoxyl protons as a singlet at 6.2τ and phenolic proton at 1.8τ.

Sodium borohydride reduction of these nitrones at room temperature yields the corresponding Schiff bases. However, if the temperature is raised, the Schiff bases are further reduced to the corresponding secondary amines[2]. Warming with zinc dust and glacial acetic acid smoothly deoxygenates the nitrones to the corresponding Schiff bases (Scheme 1). The Schiff bases and secondary amines have been identified by m. p., m. m. p.[2], elemental analysis and comparison of uv, ir, nmr and mass spectra with those of authentic samples[3].



Scheme 1

TABLE 1—VANILLIN NITRONES AND THEIR REDUCTION PRODUCTS

Sl No	R	Vanillin yield %	Nitrones m.p. °C	Deoxygenated products (Schiff bases) Yield % with $NaBH_4$ (Room temp)	with Zn/AcOH	m.p. °C	Secondary amines ($NaBH_4$ at 50-60°) yield %	m.p. °C
1.	C_6H_5	80	180	70	60	152	70	250
2.	p-$CH_3C_6H_4$	75	120	70	65	117	68	231
3	p-ClC_6H_4	82	50	72	65	123	62	189
4.	$C_{10}H_7$	60	85	65	60	157	60	185

All melting points are uncorrected
All the compounds gave satisfactory elemental analysis

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Experimental

Synthesis of C-(p-hydroxy-m-methoxyphenyl)-N-phenyl nitrone : Phenylhydroxylamine (0.1 mole) was added to vanillin (0.1 mole) taken in chloroform (250 ml) with stirring and the reaction mixture was allowed to stand at room temperature for 3-4 hr. Removal of the solvent gave crude product which was recrystallized from ethanol to yield bright yellow needles of the nitrone, m. p. 180° in 80% yield.

Reduction with sodium borohydride · Sodium borohydride (2.0 g) was added in small instalments to the nitrone (0.01 mole), prepared above, in methanol (50 ml) with stirring. The reaction mixture was allowed to stand overnight at room temperature. It was then diluted with water and extracted with chloroform. Removal of the solvent gave the crude Schiff base which was recrystallized from ethanol to yield yellow crystals, m. p. 152° in 70% yield.

If the reaction mixture was warmed to 60° the Schiff base was further reduced to secondary amine, m. p. 250° in 70% yield.

Deoxygenation with zinc dust : Zinc dust (2.0 g) was added to the nitrone (0.01 mole) taken in glacial acetic acid (10 ml) and the mixture was warmed on a water bath for 30 hr, then diluted with water and extracted with ether. Evaporation of the solvent yielded the crude Schiff base which was recrystallized from ethanol to give yellow crystals, m. p. 152° in 60% yield

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Effect of Chemicals on Protein Hydrolysate Amino Acids of Pumpkin (*Cucurbita pepo*) Seeds During Germination

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Seventeen amino acids of the acid protein hydrolysate of the germinating pumpkin (*Cucurbita pepo*) seeds treated with different chemicals were determined by circular paper chromatography. Qualitative distribution of acid hydrolysate amino acids varied a little in various treatments but appreciable quantitative change was observed during the studied span of germination. For most of the amino acids, the decrease in the protein hydrolysate amino acids during germination was associated with an increase in free amino acids. Potassium chloride has pronounced influence on nutritive value with respect to contents of essential amino acids than the mixed treatment. The results are discussed with respect to effect of soaking method, effects of chemicals on mitochondrial function and on the metabolites of the seedlings, and on the basis of mutual effects of the metabolites produced, on the contents of protein hydrolysate amino acids.

NUTRITIVE importance of proteins and dependance of animals on plants for these substances were first pointed out by Mulder[1]. Good deal of work[2-6] on the nutritive value of plant proteins has been done and it is reported that only intact proteins could be satisfactorily utilized for nutrition. It was further concluded that protein nutrition is essentially amino acid nutrition[7-10]. The essential and dietary proteins supply the building blocks for formation of tissue proteins, enzymes etc. Cereals, pulses, nuts and oilseeds form important part of Indian diet.

Studies on the effect of chemicals on germination of seeds date as far back as 1956. Swaminathan and Natrajan[11] reported that germination of several seeds was retarded when they were soaked in different oils. Very little work is reported on the effect of chemicals viz. fertilizers, growth regulators, on the chemical composition, especially on protein hydrolysate amino acids, of seeds during germination As a part of our study on the effect of fertilizers and growth regulators on morphological changes and chemical constituents of cucurbitaceae seeds we have studied the effect of some chemicals, viz. fertilizers and growth regulators, on the protein hydrolysate amino acids of pumpkin seeds and the results are reported here

Experimental

The process of pre-soaking treatment of the seeds and the mode of germination were the same as described in our previous work[12,13]. The following conditions were adopted for the soaking treatments.

Soaking period : 2 hr ; *p*H of the medium : 7 0.

Chemicals and their concentrations

A	*Fertilizers*	(mg/100 ml)
(i)	Potassium chloride (PC)	90
(ii)	Urea (Ur)	150
(iii)	Sodium phosphate (SP)	100
B.	*Growth Regulators*	(mg/100 ml)
(i)	Gibberellic acid (GA)	30
(ii)	Ascorbic acid (AA)	90
(iii)	Maleic hydrazide (MH)	50
(iv)	Sulphanilamide (SA)	50
C.	*Mixed treatment*	(mg/100 ml)
(i)	PC+AA (MT)	90+90
D	Distilled water (DW)	—

Method of extraction The material left out from 100 mg cake of the treated and the untreated (control) seeds or seedlings after extraction of free amino acids and of lower (small) peptides was taken in a round bottom flask to which hydrochloric acid (approx 10 ml, 6 0*M*) was added. Hydrolysis was crried out for 24 hr at 110°-115°. On completion of the hydrolysis the contents were cooled and the solution filtered. The filtrate containing interfering material was desalted by keeping it on regenerated I.R. 120 resin for 24 hr and then allowing it to pass through. The absorbed amino acids on the resin were eluted with 3.0 *M* ammonia solution. The elution was repeated 8 to 10 times. Ninhydrin test was done to make sure of the completion of elution. The eluent was evaporated on water bath and the thin film so obtained was dissolved in iso-propanol (10% v/v) and adjusted to a final volume of 2.0 ml for chromatographic analysis.

Chromatographic separation and estimation : The protein hydrolysate amino acids of the treated and

the control seeds at the studied periods of germination were determined by circular paper chromatography following essentially the procedure described by Krishnamurthy and Swaminathan[14]. The results were evaluated statistically and the relative errors in case of the various amino acids of different growth periods were in the range of 10 to 15%.

Results and Discussion

In the present study, in all 17 amino acids were detected in the acid protein hydrolysate. Qualitative distribution of acid hydrolysate amino acids varied a little in different treatments but the quantitative change was appreciable during the studied growth periods.

Fifteen amino acids viz., Cystine (433 μg/g), Arginine (2644 μg/g), Alanine (582 μg/g), Aspartic acid (1374 μg/g), Glutamic acid (3341 μg/g), Glutamine (3340 μg/g), Glycine (2795 μg/g), Histidine (2800 μg/g), Leucine (2538 μg/g), Tyrosine (3797 μg/g), Lysine (1163 μg/g), Methionine (488 μg/g), Phenylalanine (750 μg/g), Valine (375 μg/g) and Threonine (1269 μg/g) were found maximum in seeds treated with PC, MT, DW and the control ones They were found to decrease with the period of germination except for Cystine and Arginine which were found to decrease up to the 8th and the 10th day of germination respectively and to increase thereafter. Asparagine (2956 μg/g) and Serine (1225 μg/g) were found maximum in the Ur treatment. Asparagine content decreased up to the 10th day while that of Serine throughout the period of germination.

In the growth regulator treatments Cystine (637 μg/g), Arginine (1353 μg/g), Asparagine (2784 μg/g), Glycine (824 μg/g), Histidine (1202 μg/g), Lysine (818 μg/g), Methionine (521 μg/g) and Phenylalanine (679 μg/g) were found maximum in the AA treated seeds and their contents, except that of Arginine, decreased with the progress of germination. The amount of Arginine decreased up to the 8th day of germination but thereafter recorded an increase. Histidine content was found decreasing upto the 6th day. Thereafter, it increased up to the 8th day and again decreased up to the 12th day. In MH treated seeds, Alanine (802 μg/g), Leucine (2143 μg/g), Tyrosine (2350 μg/g) and Valine (334 μg/g) were found maximum and their contents decreased gradually over the period of germination. However, in case of Leucine a slow and steady decrease in its content was marked up to the 4th day of germination. Aspartic acid (2330 μg/g) and Glutamic acid (351 μg/g) were found maximum in GA treated seeds and their amounts were found decreasing throughout the period of germination.

From the amounts of acid hydrolysate amino acids at the reported maxima of the various free amino acids in different cases[17] it is noted that, except Asparagine in GA treatment, acid hydrolysate amino acids decreased with the periods of germination in all the cases. Asparagine content of acid hydrolysate amino acids of GA treated seeds was found increasing from the 10th day of germination. Comparing the present results with our studies on free amino acids in the seedlings during germination, it is noted that for most of the amino acids, a decrease in acid hydrolysate amino acids took place simultaneously with an increase in free amino acid. Similar observations were recorded by Hegazi[15] in case of germinating broad beans. The results suggest liberation of free amino acid as a result of hydrolysis of bound amino acid with progress of germination The varied effects of chemicals on the amino acid contents are likely to be the effects of the chemicals on mitochondria during the soaking treatment

Total amino acid (i.e FFA*+LPAA*+PHAA*) was calculated for each treatment for all the periods of germination and the following conclusions were drawn

Total amounts of Asparagine, in PC treatment, Threonine in DW treatment and Histidine in Ur and SA treatments increased throughout the periods of germination. Further, the total amount of amino acid was comparatively low than the amounts in other treatments in initial stages and in some cases even up to the end of the studied periods. The results suggest that the reported amino acids in the respective treatments must have synthesised during germination but the rate of their utilization was higher at the initial periods than at the later periods. Further, the total amounts of certain amino acids increased regularly up to certain periods of germination and then decreased as shown below

PC-Alanine (8th day), GA-Leucine (8th day); MH-Histidine (4th day), MT-Alanine, Lysine, Threonine (5th day) and Histidine, Serine (7th day) DW-Leucine (5th day) and Lysine, Glutamine, Histidine and Serine (8th day), Control-Alanine (7th day)

These results suggest that the relative rate of synthesis of the amino acids was higher than their utilization at the initial stages of germination. Subramanian[16] also reported a relative increase in protein synthesis during early germination of mung bean and runner bean Dontsova[17], while studying nitrogen compounds in the initial stages of growth of cotton seeds reported that the increase of amino acids in cotyledons was caused by proteolysis and the resulting free amino acids were used for protein synthesis The increase of total amino acids in the present study may be because of such a route.

In order to know the relative effect of chemicals, total amounts of amino acids of treated seeds were

* FAA=Free amino acid, LPAA=Lower peptide amino acid, PHAA=Protein hydrolysate amino acid

compared with the amounts of DW treated seeds for each period of germination. In the following cases, total amounts of amino acids increased in comparison to DW treated seeds throughout the periods of germination.

PC - Alanine, Arginine, Aspartic acid, Cystine, Glutamine, Glutamic acid, Glycine, Histidine, Leucine, Lysine, Methionine, Phenylalanine, Serine, Threonine, Tyrosine and Valine.

Ur - Arginine, Glycine, Serine.

SP - Arginine.

GA - Arginine, Asparagine, Glycine, Leucine and Serine.

AA - Arginine, Glycine and Valine.

MH - Arginine, Glutamine, Leucine and Serine.

MT - Arginine, Glutamine, Glycine, Leucine, Lysine and Valine.

Control - Arginine and Serine.

From the above it is concluded that either the relative rates of synthesis of the reported amino acids in specific treatments are higher than that of the DW treated seeds or their utilization in the development of the seedlings must be lower.

The trend is as under ·

PC > MT > GA > MH > Ur $\simeq$ MH > AA > Control > SP.

The trend, as shown above, suggests that PC has pronounced influence on nutritive value with respect to contents of essential amino acids than MT treatment. In case of control seeds two amino acids had a higher total than DW treated seeds which might be due to adverse effect of soaking treatment.

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Chemiluminescent Method for Determination of Low Concentration of Hydrogen Peroxide

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A chemiluminescent method for the estimation of low concentrations of hydrogen peroxide in solution phase is described This is based on the well known chemiluminescent oxidation of luminol in alkaline medium in the presence of Cu(II) as catalyst, and employs only ~2 cm^3 of sample solution. Interference due to dissolved oxygen was found to be eliminated by purging with argon gas in a cold trap at 0°. The log-log plot of chemiluminescence response versus H_2O_2 concentration was found to be linear over more than five orders of magnitude increase in the latter. The lowest detectable concentration of ~2×10^{-9} mol dm^{-3} was found to be limited not by the instrument response but by the background concentration of H_2O_2 present (even) in triple distilled water (TDW) used for making up the solutions. This could be lowered by an order of magnitude by freshly distilling the TDW over MnO_2 but was found to revert to the higher value on keeping in contact with ambient air and light. The time dependence of the chemiluminescene response was exponential, the half life being affected considerably by impurities present in the sample

THERE are a number of analytical situations requiring the accurate estimation of sub-parts per million concentration of hydrogen peroxide These are to name a few, hydrogen peroxide present in natural waters[1], in the ambient and polluted atmosphere originating from photochemical reactions[2,3], γ-radiolysis of aqueous solutions[4] and photolysis of aqueous solutions both in homogeneous solutions and catalysed at surfaces[5,6] Among the commonly used analytical methods even the most sensitive spectrophotometric ones based on the formation of intensely absorbing coloured compounds by reaction with H_2O_2 can measure concentrations down to at most 10^{-6} mol dm^{-3} under the best conditions. It is in this connection that chemiluminescent methods have attracted considerable attention. With the availability of extremely low dark current photomultiplier tubes and photon counting instrumentation it is now possible to detect very low intensities of light. Assuming a detection capability of 10^4 photons (above background) in a cell volume of 2 cm^3 and assuming chemical, quantum and geometrical efficiencies of 0.1 each, one can detect in principle a concentration as low as 10^{-14} mol dm^{-3} provided a suitable and fast (light emission being complete in about a minute) chemiluminescent reaction is available.

Luminol, (5-amino-2,3-dihydro-1,4-phthalazinedione)[1,3,8-12], *bis* (2,4,6-trichlorophenyloxalate)[13], lucigenin (N,N'-dimethyldiacridinium dinitrate)[14-17] and siloxene[18] are some of the compounds known to undergo chemiluminescent reactions with H_2O_2 and particularly the first two have been employed for the detection and estimation of low concentrations of H_2O_2. Although a photographic plate can be used as a detector of the luminescence, there are only a few reports of this[19-25] and the minimum detectable concentration was ~10^{-5} mol dm^{-3}. The photomultiplier tube is a much more sensitive light detector and the vast majority of the chemiluminescent methods for the detection of H_2O_2 have employed this device. The major reported applications have been in the fields of analysis of H_2O_2 in natural water[1] and in the ambient atmosphere[2,3,8]. Operationally, both injection[8] and continuous flow[1,3,9-12] techniques have been employed The former is simpler in practice and forms the basis of the present work, which was aimed at developing a suitable apparatus for this purpose, assessing its suitability for the analysis of low concentration of H_2O_2 in aqueous solutions and ambient air and identifying the parameters affecting the lowest detection limit.

Experimental

The apparatus employed in the present work is shown schematically in Fig 1. The sample solution is injected through a light tight injection port by means of a hypodermic syringe into the luminol+catalyst solution taken in a quartz 1 cm rectangular spectrophotometer cuvette mounted directly in front of the PMT detector in an integral light tight housing made of aluminium. The PMT detector employed is the relatively inexpensive RCA-1P28 having a photocathode response (250-500 nm) compatible with the spectrum of the light emitted in

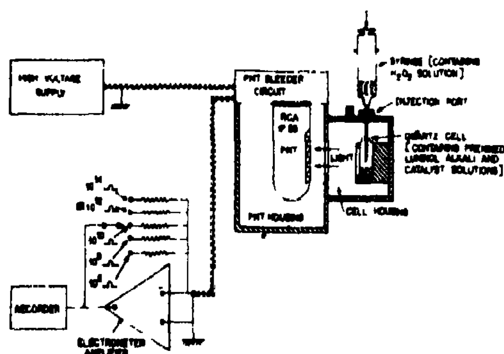


Fig 1. Block diagram of the apparatus for the study of chemiluminescent oxidation of Luminol by H_2O_2 in solution

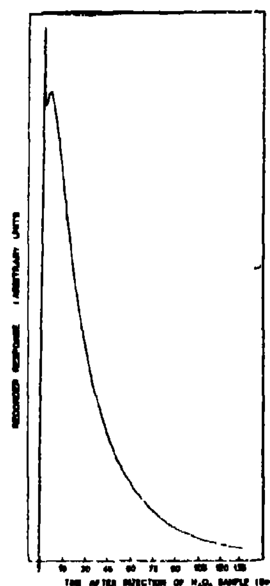


Fig. 2. Recorder trace of chemiluminescence for a 10^{-6} mol dm^{-3} H_2O_2 solution in QDW (Amplifier setting at 100 mV full scale, recorder setting at 10 mV full scale)

the reaction between H_2O_2 and luminol (λ_{max} 435 nm). The high voltage for the PMT was obtained from an 'Aplab' 7341P model power supply. The anode current from the PMT was amplified in an 'ECIL' model EA815 FET input electrometer amplifier and recorded on a 'Digilog' model 5211-5 omniscribe potentiometric strip chart recorder.

All reagent solutions were made in triple distilled water (TDW), which was routinely prepared in our laboratory by distillation of still distilled water over acid-dichromate and then over alkaline permanganate. Standard solution (10^{-2} mol dm^{-3}) of hydrogen peroxide was prepared by dilution of 6%(v/v) stock solution with TDW and checked against standardised permanganate solution by titration. Stock solutions of cupric nitrate and luminol were prepared by well established procedures[1-3,8]. Stock solutions of luminol and H_2O_2 were stored in the refrigerator to minimize decomposition over a period of time.

Our detailed studies employed Cu(II) as the catalyst. A working solution of 7.2×10^{-4} mol dm^{-3} luminol containing 4.5×10^{-6} mol dm^{-3} Cu(II) was prepared in NaOH to give a final *p*H of 12.9-13 as and when required. All other chemicals such as NaOH, $K_3[Fe(CN)_6]$, $NiSO_4$, $CoSO_4$, $FeSO_4$, NH_3 etc. were AnalaR grade and were used without further purification.

For chemiluminescence studies one cm^3 of the luminol solution containing the appropriate catalyst and *p*H adjusted to the optimum was taken in the 1 cm quartz spectrophotometer cuvette mounted in the apparatus as shown in Fig. 1. Into this was quickly (in ~5 sec) injected 2 cm^3 of the standard or test solution containing H_2O_2. The intensity of the light emitted in the chemiluminescent reaction was monitored as a function of time on the strip chart recorder. A typical recorder trace is shown in Fig. 2.

Results and Discussion

The reproducibility of the chemiluminescence response as a function of time is very good when recorder traces such as Fig. 2 are compared for the same concentration of H_2O_2. The initial response during the first five seconds after injection (shown as a very sharp peak in Fig. 2) is a composite of the response due to light emitted from the chemiluminescent reaction, light leakage during injection and mechanical disturbance due to the injection process itself, and is rather irreproducible. The subsequent decay, however, is quite reproducible. For quantitative estimation the chemiluminescence response was measured by reading the signal intensity of curves such as the one in Fig. 2 at a fixed time (15 sec) after sample injection.

Different transition metal ion catalysts were tried under conditions reported in the literature to be the most optimum for the H_2O_2-luminol chemiluminescent reaction. Among these the Cu^{2+} catalyst was found to yield the maximum chemiluminescence response and has been used throughout the rest of our work.

Although anions such as bromide have been reported[26] to enhance the chemiluminescence output of the H_2O_2+luminol reaction with Cr^{3+} as catalyst, such an effect was not observed with Cu^{2+} under the conditions employed even upto 2 mol dm^{-3} of Br^- concentration.

The variation of the chemiluminescence response with H_2O_2 concentration is shown in Fig. 3 on log-log scale. This is found to be linear over at least four orders of magnitude in H_2O_2 concentration. In fact, the upper limit is set by the maximum current readable on the least sensitive range of the amplifier used.

In the blank TDW the current due to the chemiluminescence is 1.5×10^{-8} amp (equivalent to $\sim5\times10^{-8}$ mol $dm^{-3}H_2O_2$), which is about 15 times

higher than the dark current of the 1P28 PMT employed in the present work. Therefore the present set up is inherently capable of measuring H_2O_2 concentration down to 10^{-9} mol dm^{-3}. The practical lower limit is therefore due to the background response from the TDW.

Possible sources of this background luminescence in water are presence of dissolved oxygen and H_2O_2 itself or other peroxy compounds. Chemiluminescent reaction between luminol and O_2 in

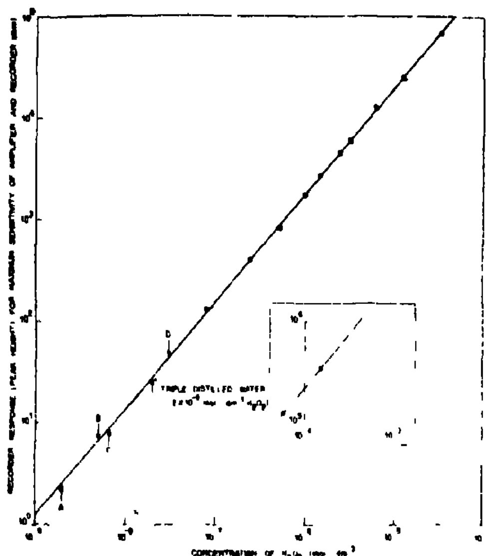


Fig 3. Calibration plot for H_2O_2 estimation in solution A-Fresh QDW, Ar saturated (kept in the dark or in ambient light for any length of time), B-Fresh as well as stored QDW (in a closed bottle) C-Fresh QDW, O_2 saturated and kept in a closed container in ambient light D-Fresh QDW kept in an open container in ambient light for 4 hr

alkaline DMSO medium has in fact been suggested[27] as a sensitive method for determination of low concentration of oxygen (as low as 10^{-11} mol dm^{-3}). The aqueous luminol + Cu(II) system employed in the present study was in fact found to give a chemiluminescence response when gaseous air or oxygen was injected. This was not due to any artefact of injection as argon gas similarly injected did not show any response. Purging of TDW with argon gas (at ~ 100 cm^3 min^{-1} with the sample immersed in ice bath to avoid loss of H_2O_2) before injection lowered the background response from the equivalent of $\sim 5\times10^{-8}$mol dm^{-3} H_2O_2 to $\sim 2\times10^{-8}$ mol dm^{-3} thus indicating that at least part of this is due to dissolved oxygen (concentration $\sim 2\times10^{-4}$ mol dm^{-3}) in TDW.

In order to find out whether the remaining part of the background response in TDW is due to H_2O_2, the TDW was subjected to one more distillation over MnO_2 and the resulting distillate (referred to as quadruple distilled water, QDW) was found to give a background response equivalent to 5×10^{-9} mol dm^{-3} H_2O_2. This further reduced to 2×10^{-9} mol dm^{-3} equivalent H_2O_2 on argon purging. The latter value together with the value of $\sim 2\times10^{-8}$ mol dm^{-3} equivalent of H_2O_2 in TDW would lead us to infer that our laboratory TDW contains 18×10^{-9} mol dm^{-3} equivalent of H_2O_2 or some other compound, capable of luminescence, being destroyed by reaction with MnO_2 at 373 K. Interestingly, the background value of 2×10^{-9} mol dm^{-3} equivalent of H_2O_2 in QDW was found to return to the TDW value when left overnight in the laboratory in the open. Detailed investigations were carried out to identify the causes responsible for this behaviour The results of these studies indicated that pure water (QDW) gets contaminated by formation of H_2O_2 (or some other species capable of undergoing a chemiluminescent reaction with luminol + Cu^{2+} system) when exposed to ambient light and air or oxygen. The extent of this was found to be more when it was exposed in an open container Although these results do not positively indicate this species to be H_2O_2, an analysis of the decay profile of the chemiluminescence response *(vide infra)* would suggest that it is most probably H_2O_2.

The chemiluminescent decay profiles for QDW and TDW injected into the luminol + Cu(II) system are compared with that for authentic H_2O_2 samples in Fig 4 on semilog scale The similarity amongst the four is quite evident Further, it is seen that although the decay is truly exponential the negative slope of the semilog plot decreases with increasing H_2O_2 concentration which would imply a somewhat complex kinetics

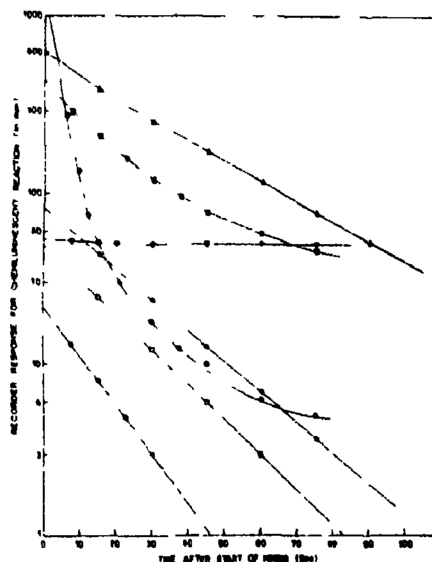


Fig 4 Semilog plot of recorder response against time for different samples of water under identical conditions ●-Fresh QDW, Ar saturated, ⊡-Fresh TDW, Ar saturated, O-8 3×10^{-8} mol dm^{-3} H_2O_2 sample, ▲-25×10^{-8} mol dm^{-3} H_2O_2 sample, ×-Tap water, ▼-DW from still, ■-O_2 saturated TDW.

Whatever be the species that is really responsible for the background chemiluminescence observed

when pure water is injected into the luminol + Cu(II) system, its implication in the analysis of low concentrations of H_2O_2 by the chemiluminescent technique is important. Thus, if we are interested in measuring concentrations of the order of 10^{-8} mol dm^{-3} we must employ QDW for preparing the H_2O_2 solution and subtract the QDW blank response from the observed response for the sample. The luminol + Cu(II) reagent solution need not be prepared in QDW as any background would have decayed prior to injection provided that the reagent has been prepared in TDW and stored for some time.

We have found the present technique to be sufficiently sensitive to measure H_2O_2 present in the ambient atmosphere[29]. Although the use of the luminol + catalyst system has been suggested to be usable for the analysis of the H_2O_2 in natural water[1], the presence of various other species can affect the chemiluminescence response in an unknown manner For example, the decay of the response for tap water was found to be nonexponential whereas the response of distilled water fresh from the still exhibited a very slow decay (see Fig. 4). These differences as compared to the decay observed in the case of authentic H_2O_2 or that present in TDW or QDW could be due to either the quenching action of impurities present in the sample or their intereferences with the reaction scheme leading to the generation of chemiluminescent species in the H_2O_2+luminol reaction It may be worth mentioning here that details of this reaction scheme as well as the identity of the luminescent species are not yet known. From the application point of view, however, it is important to establish first that the decay of the chemiluminescence response in the unknown system closely parallels that for authentic H_2O_2 before attempts are made for quantitative assay. In the absence of a convincingly good parallelism the first attempt should be to remove the interfering species by a preliminary separation scheme.

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The Effect of Some Amino Acids on the Corrosion of Aluminium in HCl Solution

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The use of some amino acids as corrosin inhibitors of aluminium in 2*N* HCl has been studied by the thermometric and weight loss methods The two methods gave concordant results. The additives caused a decrease in the maximum reaction temperature and a corresponding reduction in the reaction number (RN) Curves representing the variation of the percentage decrease in RN with the logarithm of the molar concentration of the additives were constructed. They reveal that these additives appear to lie flat on the surface of the corroding metal. Amino acids in HCl are stronger corrosion inhibitors as revealed from the results, suggesting that adsorption occurs through both the protonated −COOH and $-NH_2$ groups. The inhibition efficiency of the additives increases in the order. tyrosine>phenyl alanine> tryptophan>aspartic acid>arginine. The inhibitory character of the compounds depends upon the concentration of the inhibitor, as well as its chemical constitution.

THE corrosion of aluminium and its alloys and their inhibition by different organic inhibitors in acid solutions have been studied by several authors[1-8]. The inhibitory action of some amino acids towards corrosion of aluminium in acid solutions has been investigated[9-11].

The methods of comparing the efficiency of inhibition are numerous[12-14]. Recently Aziz and Shams El-Din[15] applied the Mylius thermometric method[16] to study the dissolution of aluminium and zinc in hydrochloric acid solutions

The object of this paper is to throw some light on the mode of adsorption of amino acids on the Al surface.

Experimental

Materials · B. D. H. grade tyrosine, phenyl alanine, aspartic acid, tryptophan and arginine were used without further purification. The acid (2*N* HCl), degreasing mixture and additive solutions were prepared as previously described[17].

The impurities in aluminium sheet was as follows Si, 0.15 ; Fe, 0.19 ; Mn, 0.005 ; Mg, 0.1 ; Cu, 0 02%. Their dimensions were 10×100×1 5 mm. The sheets were degreased and cleaned as previously described[18].

Apparatus and working procedures. The reaction vessel used was basically the same as that described by Mylius[16]. According to this method, a test piece of the metal under study, measuring 10×100×1.5 mm, is immersed in 15 ml of 2*N* HCl in presence and in absence of the additives and the temperature of the system is followed as a function of time. The temperature rises, first slowly and then rapidly, to attain a maximum value and then decreases again. The reaction number RN is defined as

$$RN = \frac{T_m - T_i}{t} \ °C/min.$$

where T_m and T_i are the maximum and initial temperatures respectively, and t is the time in minutes from the start of the experiment till the attainment of maximum temperature. The initial temperature was always 25±0 1°

The procedure followed in weight loss measurements was similar to that reported previously[18]. The percentage inhibition of the additives was computed as ·

$$100\left(\frac{W_{free} - W_{add}}{W_{free}}\right)$$

where W is the loss in weight of the test piece.

Results and Discussion

Thermometric measurements : The dissolution of Al in 2*N* HCl was accompanied by temperature change This temperature change was followed in the absence and in the presence of different concentrations of the following amino acids viz., tyrosine, phenyl alanine, tryptophan, aspartic acid and arginine

In all cases the dissolution of Al in acid is characterized by initial slow rise in temperature followed by a sharp rise and finally decrease after attaining a maximum value. The maximum temperature (T_m) measured in the free acid is 16.2° and is attained after 20 min, while the T_m in the presence of the additives used are lower and are attained after a longer time. This indicates that additives behave as inhibitors for the dissolution of aluminium in 2*N* hydrochloric acid, presumably by their adsorption on the surface of the metal.

The present thermometric curves allow distinction between weak and strong adsorption[11]. Weak adsorption is noted for all amino acids used. The curves in Fig. 1 represent this adsorption in the presence of tryptophan, in which the maximum temperature slightly decreases whilst the time necessary to reach T_m increases.

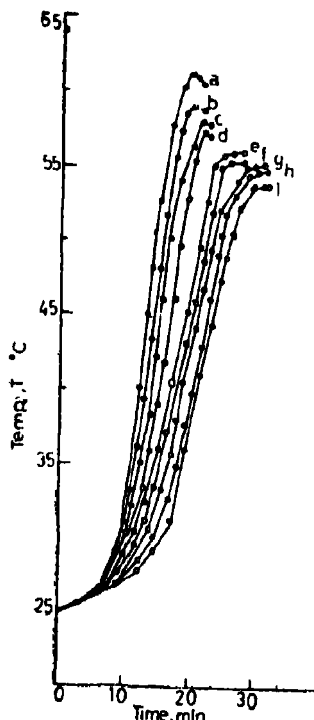


Fig. 1. Temp-time curves obtained in absence and in presence of varying concentration of tryptophan.

(a) free acid (b) $10^{-6}M$ (c) $10^{-5}M$ (d) $10^{-4}M$ (e) $5\times10^{-4}M$ (f) $10^{-3}M$ (g) $5\times10^{-3}M$ (h) $10^{-2}M$ (i) $5\times10^{-2}M$

The fact that the compounds studied bring about a decrease in RN indicates that they act as inhibitors. The results recorded in Table 1 reveal that the efficiency of corrosion inhibition as determined from the percentage reduction in RN varies with both the concentration and the type of the amino acid used.

TABLE 1—EFFICIENCY OF CORROSION INHIBITION AS DETERMINED BY PERCENTAGE REDUCTION IN RN

Concentration of the additive in M	%Reduction in RN				
	Tyrosine	Phenyl alanine	Tryptophan	Aspartic acid	Agrinine
10^{-6}	—	23.8	20.1	12.2	3.8
10^{-5}	64.4	33.1	30.1	13.2	8.3
10^{-4}	66.6	40.4	45.0	17.9	10.5
5×10^{-4}	67.7	62.8	—	28.4	16.6
10^{-3}	73.0	72.5	70.6	23.0	22.1
5×10^{-3}	79.6	78.8	71.0	41.2	31.0
10^{-2}	80.6	79.1	71.8	43.6	35.9
5×10^{-2}	92.0	85.0	80.8	46.4	39.1

The inhibition efficiency of the additives increases in the order : tyrosine > phenyl alanine > tryptophan > aspartic acid > arginine.

A plot of the percentage reduction in RN against log C is in fact similar to an adsorption isotherm (Fig. 2.). The points of inflexion in the percentage reduction in RN vs log C curves occur at $C=10\times10^{-4}M$ and bear no relation to their chain length. This behaviour is explainable on the basis of a one-step adsorption process. The same conclusion can be obtained on plotting log time delay (Δ t) vs log concentration (C) (Fig. 3) [time delay (Δ t) is the difference between T_m in presence of the additive and T_m in absence of the additive]. These curves consist of an initial ascending portion which passes to a region of constancy indicating the completion of a monolayer of the adsorbate.

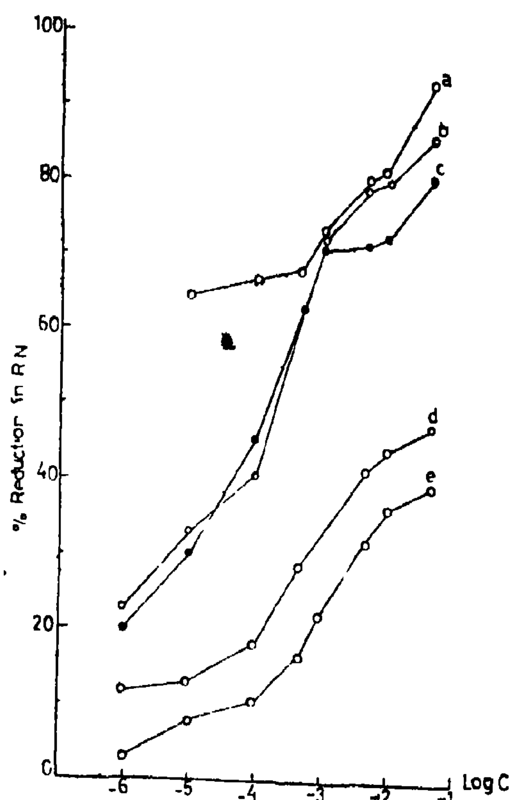


Fig. 2. % Reduction in RN-log C curves for all additives used.

(a) Tyrosine (b) Phenyl alanine (c) Tryptophan (d) Aspartic acid (e) Arginine

Effect of chemical composition : It is clear that in the strong acid solution under consideration both the carboxylic and the amino groups of the additives are expected to be fully protonated. Zwitter ion formation does not, therefore, contribute significally to the actual state of the molecules in solution. Both functional groups adsorb on the cathodic sites of the corroding metal. Fig. 4 represents

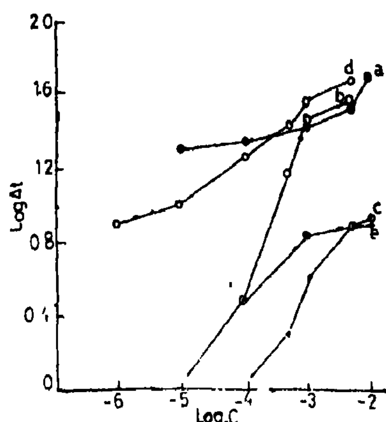


Fig 3. Log Δt-log C curves for the additives used.

the schematic presentation of the mode of adsorption of amino acids. The results indicate that the

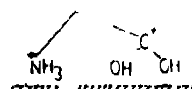


Fig. 4

neutral amino acids (tyrosine, phenyl alanine, tryptophan) inhibit the corrosion more than the acidic amino acids (aspartic acid) and also the basic ones (arginine). Tyrosine inhibits more than phenyl alanine and tryptophan because of the presence of $-OH$ group in the p-position which increases the interaction of the delocalized π electrons with the metal surface, enlarging the coverage and enhancing the inhibitory effect at very low coverage while in tryptophan, the adsorption is via both $-NH_2$ and $-COOH$ groups, the rest of molecule being protruded in solution and free to rotate. In aspartic acid, the adsorption is through $-NH_2$ and one COOH groups while the other $-COOH$ is perpendicular to the metal surface. In arginine, the presence of unsaturation decreases the interaction of the delocalized π electrons with the metal surface and hence it gives low inhibition efficiency.

Weight loss measurements: This method was used in order to prove that the amino acids used, retard the corrosion of aluminium. The loss in the weight of aluminium strips in $2N$ HCl in the absence and in the presence of different concentrations of the additives was determined over a period of 75 min. The weight loss is plotted as a function of time for tryptophan (Fig. 5). The curves are characterized by an initial slow increase in weight loss (due to the originally formed oxide film on the surface of the metal) followed by a sharp rise (due to the breakdown of the formed oxide film on beginning of the attack). The curves obtained in presence of the additives fall below that of the free acid. It was shown that the weight loss of aluminium depends on both the type and concentration of the additives in the same way as the percentage reduction in RN does.

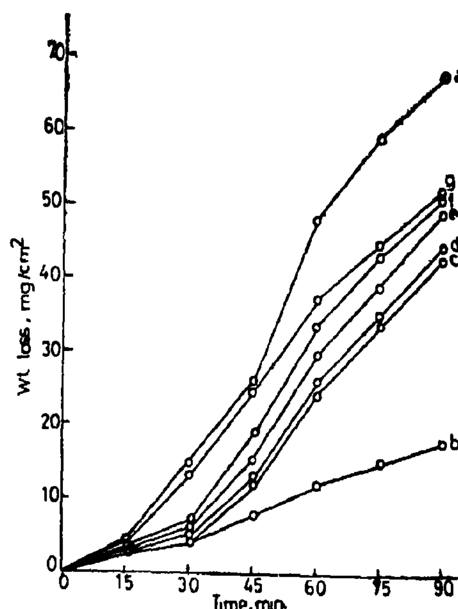


Fig. 5. Weight loss-time curves for tryptophan.
(a) free acid (b) $10^{-2}M$ (c) $5\times10^{-3}M$ (d) $10^{-3}M$ (e) $5\times10^{-4}M$ (f) $10^{-4}M$ (g) $10^{-5}M$

Duplicate experiments were carried out and weight losses averaged. In Table 2 the inhibitors examined are arranged in the order of increasing inhibition efficiency. It also shows that the compounds used follow the same order when arranged according to the percentage reduction in RN at the same concentration of inhibitor ($10^{-2}M$) and after 60 min from the start.

Table 2—Comparison between Efficiency of Inhibitors as Determined by Thermometric and Weight Loss Techniques in Acid Solution

Substance	%Reduction in RN	%Inhibition
Free acid	—	—
Tyrosine	80.6	81.2
Phenyl alanine	79.1	80 1
Tryptophan	71.8	73.4
Aspartic acid	43 6	45.7
Arginine	35.9	36 7

Thus the same order of inhibitory action is obtained by weight loss and thermometric measurements. This indicates the validity of the results obtained by the two different methods for the use of amino acids as corrosion inhibitors of Al in $2N$ hydrochloric acid solution.

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Extractive Spectrophotometry of Palladium(II) and Ruthenium(III) with Phenanthraquinone Monothiosemicarbazone

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A procedure is described for the extractive spectrophotometric determination of palladium and ruthenium with phenanthraquinone monothiosemicarbazone. Palladium forms a 1 : 2 complex which is soluble in chloroform and has an absorption maximum at 600 nm when extracted from 1*M* acetic acid solution. Ruthenium forms a 1 : 2 complex which is soluble in chloroform and has an absorption maximum at 660 nm when extracted from 2*M* acetic acid solution. Both complexes are stable and conform to Beer's Lambert law. The molar absorptivity (and Sandell's sensitivity) for palladium and ruthenium are 2.2×10^4 l mole^{-1} cm^{-1} (0.04 μg/cm^2) and 4.74×10^4 l. mole^{-1} cm^{-1} (0.02 μg/cm^2) respectively. The proposed method is suitable for detection and determination of palladium and ruthenium in the presence of associated metal ions. The results of the analysis of synthetic mixtures are reported.

PHENANTHRAQUINONE monothiosemicarbazone (PQMT) has been used for the spectrophotometric determination of traces of copper in ferrous and nonferrous alloys[1]. Extension of this study revealed that PQMT could be used for the extractive spectrophotometric determination of palladium(II) and ruthenium(III).

Experimental

Apparatus and reagents. A Zeiss spectrophotometer (Jena) with 1 cm silica cell was used for the absorbance measurements. The stock solutions of palladium ($1 \times 10^{-2}M$) and ruthenium ($1.68 \times 10^{-2}M$) were prepared by dissolving analytical grade palladium chloride and ruthenium trichloride (Johnson Matthey, London) and standardized by known methods. The solutions of lower concentration were prepared by appropriate dilution of the stock solutions.

Phenanthraquinone monothiosemicarbazone (PQMT) was synthesized by the reported method[2] and 0.01% (w/v) or 0.06% solution in dimethyl formamide (DMF) was used for palladium and ruthenium estimations respectively. All other chemicals were of analytical grade.

Procedure : A 10 ml aliquot of solution containing 25 to 180 μg of palladium, 2 ml of 0.01% PQMT in DMF and acetic acid (1*M*) is taken and extracted for 15 sec with two 5 ml portions of chloroform. The organic phase is separated, dried with anhydrous sodium sulphate and the absorbance is measured at 600 nm against the reagent blank prepared in the same manner. Similarly, 10 ml aliquot of solution containing 10 to 150 μg of ruthenium, 4 ml of 0.06% PQMT in DMF and acetic acid (2*M*) is taken. The mixture is heated for 10 min in a boiling water bath, cooled and extracted for 15 sec with two 5 ml portions of chloroform. The chloroform layer is separated, dried with anhydrous sodium sulphate and the absorbance of the green coloured complex is measured at 660 nm against the reagent blank prepared analogously. The palladium and ruthenium contents are computed from the calibration graph.

Results and Discussion

The extraction behaviour of palladium and ruthenium from various acidic media is shown in Table 1. Pd-PQMT complex quantitatively extracts into chloroform from 1-3 *M* acetic acid, hydrochloric acid and perchloric acid solutions. Ru-PQMT complex, however, extracts from 2-3 *M* acetic acid, 1-3 *M* hydrochloric acid and 1-2 *M*

TABLE 1—EXTRACTION OF PALLADIUM(II) AND RUTHENIUM(III) COMPLEXES AS A FUNCTION OF ACIDITY

Acid		%Extraction		Distribution ratio D	
		Pd	Ru	Pd	Ru
CH_3COOH	0 25*M*	87 7	80 0	7.10	4 0
	0 50*M*	95.0	87.5	19 23	7 0
	1 00*M*	100	92 3	∞	13 0
	2-3*M*	100	100	∞	∞
	4 00*M*	82.7	84 7	4 8	5 6
HCl	0 5*M*	60 0	85 6	4.0	6.0
	1-3*M*	100	100	∞	∞
	4.0*M*	83 4	88 9	5 0	8 1
$HClO_4$	0.5*M*	76.0	83.4	3 1	5.0
	1-2*M*	100	100	∞	∞
	3.0*M*	100	96 4	∞	26.7
	4.0*M*	92 0	90 0	11.5	9.0
H_2SO_4	0.5*M*	52 4	40 0	1 1	0 67
	1 0*M*	56 0	45.2	1.27	0 83
	2-3*M*	60 0	37.3	1.5	0.60
HNO_3	0.5*M*	30 1	15.3	0 4	0 19
	1 0*M*	38 2	20 0	0.61	0.25
	2-3*M*	34.0	17.0	0.50	0.20

perchloric acid solutions. Nitric acid and sulphuric acid media are unsuitable for extraction of both palladium and ruthenium. The extraction period for quantitative extraction of both Pd and Ru is only 15 sec. The extracted palladium and ruthenium complexes absorb at 600 and 660 nm respectively (Fig. 1) and adheres to Beer's law over the concentration range of 25 to 180 μg of Pd and 10-150 μg of Ru/10 ml of organic phase. The molar absorptivity and Sandell's sensitivity for Pd-PQMT complex is 2.2×10^3 l. $mole^{-1}$ cm^{-1} and 0.04 $\mu g/cm^2$ respectively. For Ru-PQMT complex, the molar absorptivity and Sandell's sensitivity is found to be 4.74×10^3 l. $mole^{-1}$ cm^{-1} and 0.02 $\mu g/cm^2$ respectively. The colour of the complexes is stable for 24 hr. 2 ml of 0.01% PQMT solution and 4 ml of 0.06% PQMT solution in DMF is enough for quantitative extraction of Pd and Ru respectively. Excess of reagent had no adverse effect on the intensity of the colour.

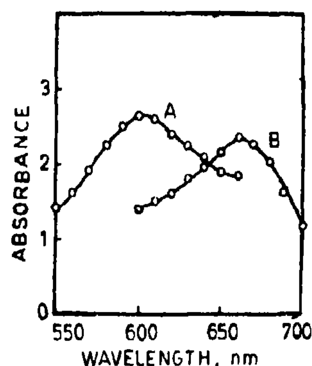


Fig. 1. Absorption spectra of :
(A) Palladium complex and
(B) Ruthenium complex

The solubility of the palladium and ruthenium complexes was tried in different organic solvents. Results in Table 2 show that the only effective solvents for palladium and ruthenium extractions are chloroform, methyl isobutyl ketone (MIBK), isoamyl alcohol and ethyl acetate.

TABLE 2—EXTRACTION OF Pd-PQMT AND Ru-PQMT COMPLEXES WITH VARIOUS ORGANIC SOLVENTS FROM 2M ACETIC ACID SOLUTION

Solvent	Extraction %	
	Pd	Ru
Carbontetrachloride	0	0
Benzene	52	50
Toluene	48	38
Xylene	45	40
Chloroform	100	100
Isoamyl alcohol	100	100
MIBK	100	100
Ethyl acetate	100	100

Effect of foreign ions : A number of representative ions were tested for their interference in the determination of palladium (100 μg) and ruthenium (50 μg) by the recommended procedure. The tolerance limit was set at the amount required to cause $<$ 1% error in metal determination. In palladium estimation, ions tolerated are monovalent silver (5 mg), bivalent copper (5 mg), cobalt (5 mg), zinc (5 mg), manganese (5 mg), tin (2 mg), nickel (5 mg), mercury (2.5 mg), trivalent aluminium (2 mg), bismuth (100 μg), chromium (2.5 mg), gold (2 mg), antimony (1 mg), ruthenium (3 mg), rhodium (3 mg), iridium (250 μg), iron (2.5 mg), lanthanum (2 mg), quadrivalent tin (150 μg), platinum (3 mg), thorium (250 μg), selenium (500 μg), tellurium (100 μg), pentavalent vanadium (2 mg), hexavalent uranium (5 mg), chromium (5 mg), osmium (2.5 mg), tartarate (3 mg), citrate (4 mg), ascorbate (5 mg), EDTA (5 mg), phosphate (5 mg), fluoride (5 mg), bromide (5 mg) and chloride (5 mg). Lead (500 μg) requires masking with EDTA. Notable interference is cadmium. Similarly in ruthenium extractions, tolerable ions include Ag (500 μg), Mn (600 μg), Sn (1000 μg), Ni (1500 μg), Pd (100 μg), Pb (1500 μg), Al (2000 μg), Cr (300 μg), Au (500 μg), Sb (600 μg), Rh (300 μg), Ir (200 μg), La (2500 μg), Sn(IV) (500 μg), Pt (1500 μg), Th (100 μg), Se (300 μg), Te(500 μg), V (500 μg), U (500 μg), Os (250 μg), tartarate (1000 μg), citrate (1000 μg), ascorbate (2500 μg), EDTA (1000 μg), phosphate (800 μg), fluoride (5000 μg), bromide (1500 μg) and chloride (2000 μg). Mercury (1000 μg) and Iron (500 μg) require masking with fluoride. 1000 μg of Zn and 300 μg of copper also tolerate if masked with citrate and EDTA respectively. Notable interference in ruthenium determinations are cobalt, cadmium, bismuth and chromium(VI).

Composition of extracted species : The composition of Pd-PQMT and Ru-PQMT complexes were determined by Job's continuous variation method[3] and the mole ratio method[4]. Both methods indicate the formation of a 1 : 2 complex. The dissociation constants, K, of the complexes were found to be 1.38×10^{-3} for Pd and 4.2×10^{-10} for Ru.

TABLE 3—ANALYSIS OF SYNTHETIC MIXTURES*

Composition of mixtures/μg	Palladium recovered %	Ruthenium recovered %	Relative error %
(1) Pd 100, Pt 1000, Ru 1000	99.0	—	1.0
(2) Pd 100, Co 1000, Ni 1000, Fe 1000	98.5	—	1.5
(3) Pd 100, Ir 100, Au 100, Pt 100	98.0	—	2.0
(4) Ru 50, Os 100 Pd 100, Rh 100	—	98.5	1.5
(5) Ru 50, Au 100, Os 100	—	97.0	3.0
(6) Ru 50, Os 100, Rh 100, Ir 100	—	99.2	0.8

* Triplicate analysis.

The method is suitable for determination of palladium in presence of Pt, Ru, Rh, Co, Ni, Fe, Ir and Au and that of ruthenium in synthetic mixtures containing Os, Pd, Rh, Au and Ir (Table 3).

The precision of the method is fairly good. The standard deviation for Pd (100 μg) and Ru (50 μg) is 0.003 whereas coefficient of variation is 1.5 and 1.2% respectively.

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NOTES

Dioxouranium(VI) Heterochelates

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ALTHOUGH there has been considerable research interest on the homochelates of dioxouranium(VI) very little has appeared on the heterochelates of dioxouranium(VI)[1]. In this paper we describe the synthesis and characterization of new dioxouranium(VI) heterochelates, the ligands used being *ortho*phenanthroline, 2,2'-dipyridyl, 3-aminopyridine, *ortho*phenylenediamine, ethylenediamine, trimethylenediamine, tetramethylenediamine, hexamethylenediamine and the Schiff base derived from benzoylhydrazide and salicylaldehyde There has also been considerable research on the Schiff base complexes of first transition series metal ions But comparatively little work has been reported on such complexes of second and third transition series metal ions[2,3]. It is hoped that the present study would contribute to the development of the chemistry of heterochelates.

Experimental

Materials : Uranylacetate dihydrate was obtained from Hopkins and Williams (London). Salicylaldehyde, ethylenediamine, *ortho*phenanthroline and 2,2'-dipyridyl were the products of Sarabhai M Chemicals. Trimethylenediamine, tetramethylenediamine, hexamethylenediamine and *ortho*phenylenediamine were procured from Fluka AG (Switzerland).

Methods : Uranium analysis was done gravimetrically as U_3O_8 after decomposing the complex with conc. HNO_3 and then igniting. Nitrogen was determined microanalytically. The Schiff base and aromatic amine were estimated quantitatively by bromometric titration technique. Conductance measurements were done in DMSO using a Toshniwal Conductivity Bridge (type CL01-02A). Mol. wt. was determined by the Rast method[4] using diphenyl as the solvent. IR spectra were recorded in KBr pellets using a Beckman IR20 spectrophotometer calibrated with polystyrene. Reflectance spectra were recorded on a Beckman DU recording spectrophotometer attached with the reflectance arrangement.

General method of synthesis of heterochelates : A methanolic solution of uranylacetate dihydrate (0.84 g ; 0.002 mole in 10 ml) was added to a methanolic solution of the Schiff base (0.48 g ; 0.002 mole in 10 ml) and the mixture was refluxed on a waterbath for 2 hr. To this solution a methanolic solution of the appropriate bidentate amine (0.002 mole in 10 ml) was added and the mixture was refluxed for 1 hr. The separated precipitates were suction filtered, washed with methanol and dried *in vacuo* at room temperature Yield 80%.

Results and Discussion

The dioxouranium(VI) heterochelates have been synthesized by employing a preparative method in which the possibility of expansion of coordination number of the homochelates has been utilised. The heterochelates are formed by the reaction of bidentate ligands on six-coordinated complex of the type $UO_2L\ CH_3OH$ (where L = tridentate dibasic Schiff base) prepared *in situ* It may be noted that the *in situ* method of preparation of heterochelates described in this paper is simpler and less time consuming as it does not require the isolation of the homochelates in the solid state The heterochelates are of the type $UO_2L(AA)$ (where LH_2 = sal-benzoylhydrazide, AA = *ortho*phenanthroline, 2,2'-dipyridyl, 3-aminopyridine, *ortho*phenylenediamine, ethylenediamine, trimethylenediamine, tetramethylenediamine or hexamethylenediamine). The molecular weight measurements indicate that the complexes are monomers. They are non-electrolytes (Λ_M = 2-8 ohm^{-1} cm^2 mole^{-1}) and diamagnetic as expected for $5f^0$ uranium(VI).

The Schiff base exhibits the ν(C=O) stretch at 1668 cm^{-1} which disappears in the complexes due to enolisation and consequent coordination of oxygen atom. The ν(C=N) stretch of the Schiff base occurs at 1610 cm^{-1} and this band is lowered by 5-15 cm^{-1} in the complexes. The ν(C=N) stretch of *ortho*phenanthroline, 2,2'-dipyridyl and 3-aminopyridine occurs at 1558, 1582 and 1590 cm^{-1} respectively[6,7] In the heterochelates, this band shifts to higher energy by 10-35 cm^{-1}. This negative or positive shifts in ν(C=N) stretch is indicative of nitrogen coordination of the Schiff base[5] and heterocyclic amines[6]. The $\delta(NH_2)$ band of ethylenediamine, trimethylenediamine, tetramethylenediamine, hexamethylenediamine, *ortho*phenylenediamine and 3-aminopyridine occurs at 1620, 1620, 1620, 1620, 1640 and 1590 cm^{-1} respectively and in the complexes this band shifts to lower energy by 10-25 cm^{-1} and in some cases merges with the ν(C=N) stretch. This indicates coordination through the nitrogen atoms of the

TABLE 1—ANALYTICAL, MOLECULAR WEIGHT AND INFRARED SPECTRAL DATA OF DIOXOURANIUM(VI) HETEROCHELATES[a,b]

Complex	Found (Calcd.)% U	N	ligand[c]	Mol wt	ν_s(OUO)	ν_{as}(OUO)	f_{UO} m dynes/Å	R_{UO} Å	ν(C–O) (phenolic)	ν(C=N)
UO_2(sal-BHZ)(en)	42.15 (41.90)	10 05 (9.86)	41 43 (41 90)	511 (568)	800	880	6 43	1.75	1550	1595
UO_2(sal-BHZ)(tn)	41.12 (40 89)	9 83 (9 62)	41 05 (40.89)	608 (582)	800	880	6 43	1 75	1555	1595
UO_2(sal-BHZ)(bn)	39 75 (39 93)	9.13 (9 35)	39 38 (39.93)	573 (596)	810	890	6 58	1 75	1555	1595
UO_2(sal-BHZ)(hn)	38 06 (38 14)	8 65 (8 97)	37 77 (38 14)	647 (624)	815	895	6 65	1 74	1555	1600
UO_2(sal-BHZ)(phen)	38 49 (38 64)	9.33 (9 09)	56.13 (56 17)	603 (616)	815	895	6.65	1.74	1555	1595
UO_2(sal-BHZ)(dipy)	35 74 (35 84)	8 26 (8.43)	59 40 (59 31)	642 (664)	820	900	6 73	1.74	1545	1600
UO_2(sal-BHZ)(ampy)	39 35 (39.53)	9 12 (9 30)	55 06 (55 15)	584 (602)	810	890	6 58	1 75	1545	1595
UO_2(sal-BHZ)(o-phen)	34 31 (34 59)	8 28 (8 14)	60 49 (60 76)	701 (688)	820	900	6 73	1 74	1545	1600

(a) Abbreviations sal – salicylaldehyde, BHZ = benzoylhydrazide, en = ethylenediamine tn = trimethylenediamine, bn – tetramethylenediamine, hn = hexamethylenediamine, phen – *ortho*phenylenediamine, dipy – 2,2′-dipyridyl, o-phen – *ortho*phenanthroline and ampy = 3-aminopyridine

(b) All ir bands in cm^{-1}

(c) Schiff base and aromatic amine

amines The heterochelates exhibit a strong band at 1545-1555 cm^{-1} due to ν(C - O) (phenolic) and this band is observed at lower energy (1535 cm^{-1}) in the Schiff base This is indicative of coordination of the phenolic oxygen atoms of the Schiff base Thus the Schiff base is behaving as tridentate ligand coordinating through ONO donor atoms The ir and analytical data alongwith the valence requirement of the metal ion indicate that the Schiff base is acting as a dibasic ligand

All the complexes exhibit the ν_s (O - U = O) and ν_{as}(O – U = O) in the range 800-820 and 880-900 cm^{-1} respectively[8] In the complex UO_2(sal-benzoylhydrazide) CH_3OH these frequencies are observed at 830, 910 cm^{-1}. The observed negative shift of the ν_s (O = U = O) and ν_{as} (O – U = O) bands in the heterochelates in comparison to the homochelate is due to the increase of electron density on the uranium atom This causes an increase in the repulsive forces with the non-bonding electrons of the atoms of UO_2 moiety and thus the U - O bond weakens. The force constant (f) values were calculated by the method of McGlynn *et al*[8] and these values agree well with those reported in the literature[8,9] The U – O bond length (R) was calculated using the relation $R_{U-O} = 1\ 08\ f^{-1/3} + 1\ 17$ and R lies in the range 1 74-1.75Å in agreement with the reported values (1 60-1 92Å)[8,9] The plot of ν_s vs ν_{as} gives a straight line with slope of 1 0 (calculated by the method of least square) and intercept of – 80. In case of linear O = U = O moiety, with no interaction of the ligands, the ν_s and ν_{as} are related by the equation[8] $\nu_s = (1+2\ M_O/M_U)^{-\frac{1}{2}} \nu_{as}$ (where M_O and M_U are the atomic mass of oxygen and uranium) which predicts a slope of 0 94. The higher value of the slope and the negative value of the intercept are due to the strong interaction of the equatorial ligands on UO_2 moiety The complexes exhibit a band in the range 20000-21000 cm^{-1} due to the ${}^1E_g^+ \rightarrow {}^3\pi_u$ transition typical of OUO moiety

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Synthesis and Characterization of Mixed Ligand Complexes of Divalent Nickel

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THE coordination tendencies of β-diketo compounds are well established. These ligands are widely used to prepare the new mixed ligand complexes, where they may act as primary or secondary ligand. They often behave as bidentate ligand but sometimes can also act as unidentate ligand e g, $Me_2Si(acac)_2$[1]. The chemistry of metal β-diketonates is well documented[2,3]. The present study describes the complexes formed by the interaction of *bis*-(ethylenediamine or propylenediamine) nickel(II) chloride with β-diketone or β-ketoesters and characterized by analytical, magnetic and spectral data.

Experimental

Bis(ethylenediamine) and *bis*(propylenediamine) nickel(II) chloride were prepared according to method described in the literature[4] Preparative work was carried out under absolute anhydrous conditions. β-keto compounds were dried by the literature procedures

Preparation of the complex bis(ethylenediamine) (acetylacetonato) nickel(II) chloride. *Bis*(ethylenediamine) nickel(II) chloride (0.001 mole) with an excess of acetylacetone in absence of any other solvent, was refluxed till a clear green solution was obtained On keeping the clear solution overnight a crystalline compound separated out. This was filtered and the adsorbed solvent was removed under reduced pressure at room temperature. The crystalline compound was washed with ethanol-ether mixture and dried *in vacuo*

Similar methods were used for the preparation of the rest of the complexes.

Physical measurements · The electronic spectra of these complexes were recorded on Carl VSU-2 spectrophotometer using Carl Zeiss alcohol solution. The ir spectra were recorded on Perkin Elmer 521 spectrophotometer in the region 4000-400 cm^{-1} in KBr pellet. Magnetic susceptibilities were measured at room temperature by using Gouy's method in alcohol solution. Analytical estimations were carried out by the standard methods.

Results and Discussion

All the complexes were found soluble in methanol and ethanol. It has been observed that when reactions are carried out under anhydrous condition, the $-NH_2$ group of diamine does not condense with carbonyl group of β-keto compound. On the other hand, it has been observed in several cases that the carbonyl group of β-keto compound condensed with $-NH_2$ group to generate an azomethine group if the reaction is carried out in aqueous media[5].

The observed and calculated elemental analysis show close resemblance within the experimental limits The values of the magnetic moment (μ_{eff}) (Table 1) of these complexes are in the range 2.94 B. M. to 3.20 B. M suggesting the presence of two unpaired electrons; hence the complexes are spin free which most probably have near octahedral stereochemistry.

The observed spectral data and the ligand field parameters are given in Table 1 Three bands have been observed in each complex in the region 5570 cm^{-1} to 11050 cm^{-1}, 15870 cm^{-1} to 18020 cm^{-1} and 25510 to 30300 cm^{-1} The ground state of octahedral d^8 system is A_{2g} and the above spin allowed transitions assuming distorted octahedral geometry of the complexes may be assigned $3A_{2g}(F)\rightarrow3T_{2g}(F)$, $3A_{2g}(F)\rightarrow3T_{1g}(F)$ and $3A_{2g}(F)\rightarrow3T_{1g}(P)$ in order of increasing energy and labelled as ν_1, ν_2 and ν_3 respectively. For d^8 complexes with O_h symmetry, Lever[6] observed that the configuration interaction between $T_{1g}(P)$ and $T_{1g}(F)$ excited states lower the ratio ν_2/ν_1 from the theoretical value 1 8 to 1 5-1 7 which is in conformity with our experimental data supporting the distortion in octahedral geometry. Various numerical fitting methods for d^8 ion suggested by Koning[7] have been applied The calculated values are in good agreement with the experimental values The values of β show a trend of covalent bonding in these complexes The value of nephelauxetic parameter (h_x) and crystal field parameter (f)[8] for the ligands used give the comparative estimation of the value of covalence character $(1-\beta)$ and the value of Dq in the metal complexes respectively The spectral parameters 10Dq, B, Dq/B, β and ν_2/ν_1 are also consistent with the proposed distorted octahedral stereochemistry[7,9]

In the mixed ligand complexes of acetylacetone and β-ketoester there will be considerable electron release resulting in the shifting of C–O and C–C bands to higher frequency when additional ligand is bonded to metal ion while the electron drain from the ring system shifts the above bands to lower frequency. Hence it is very difficult to explain precisely the shifting of the band either to higher or lower frequency region But the definite and marked shifts in the position of the bands from the parent complex show the bonding of the second ligand to metal. This can be seen by comparing the respective modes given in Table 2.

The change in νC—C—C stretching mode due to addition of acetylacetone indicate the change in the angle of C—C—C bond i.e. double bond single bond interaction changes. This indicates that most of the frequency shift in the strained ring carbonyl are due to the changes in the geometry rather than large changes in force constant[10]. Perusal of

TABLE 1—MAGNETIC DATA, ELECTRONIC BANDS AND SPECTRAL PARAMETERS (cm^{-1})

Complex	μ_{eff} B.M.	ν_1	ν_2	ν_3	10Dq	B	β	Dq/B	ν_2/ν_1	h_x	f factor
$[Ni(en)_2(acac)]Cl$	2.94	10990	18020	30300	10990	1023	0.97	1.06	1.63	0.25	1.26
$[Ni(en)_2(MAA)]Cl$	3.19	11050	17860	29240	11050	930	0.88	1.18	1.61	1.00	1.27
$[Ni(en)_2(EAA)]Cl$	3.08	10420	16980	28410	10420	942	0.90	1.10	1.63	1.83	1.20
$[Ni(pn)_2(acac)]Cl$	3.20	9570	15870	27550	9570	980	0.93	0.97	1.65	0.58	1.10
$[Ni(pn)_2(MAA)]Cl$	3.01	10530	16180	25510	10530	673	0.64	1.56	1.53	3.00	1.21
$[Ni(pn)_2(EAA)]Cl$	3.10	10100	16000	25970	10100	778	0.74	1.29	1.58	2.17	1.16

TABLE 2—SIGNIFICANT IR BANDS OF MIXED LIGAND COMPLEXES

$[Ni(en)_3]Cl_2$	$[Ni(en)_2(acac)]Cl$	$[Ni(en)_2(MAA)]Cl$	$[Ni(en)_2(EAA)]Cl$	$[Ni(pn)]Cl_2$	$[Ni(pn)_2(acac)]Cl$	$[Ni(pn)_2(MAA)]Cl$	$[Ni(pn)_2(EAA)]Cl$	Assignments
3410w	—	3420s	—	—	3400sh	—	—	
3320sh	3380w	3310s	3370w	3335w	—	—	—	$\nu N-H$
3280w	—	—	3280w	3300w	—	3300mbr	3300mbr	
3240w	3240sh	3230w	3240sh	3260w	3240sh	—	—	$2(\delta NH_2)$
2930s	2930m	2960s	2980s	2970s	2980m	2960w	2960w	$\nu_{as}(C-H)$
2870m	2890w	2840w	2980w	2890m	2880m	—	—	$\nu_s(C-H)$
—	1650sh	1650s	1630sh	—	1650w	1680w	1690sh	$\nu C-O$
—	1620w	1620w	1620s	1625w	1630sh	1630m	1620w	$\nu C-C$
1585s	1605w	1585w	1600w	1600s	1610s	1620s	1580w	δNH_2
	1515s	1500s	1570s	1505vw	1570s	1515sh	1515w	$\nu_s(C-N)+\nu_s(N-H)$
1450w	1465w	1470w	—	1460s	1460s	1455m	1455w	CH_2 and CH_3 asym. deform.
1270m	1265s	1280s	1250s	1275s	1265s	1265w	—	$\nu_s(C-N)$
—	1205m	1215s	—	1200m	1200s	1200w	1200w	
1140w	1155w	1170s	1175w	1160m	—	1145w	1145w	CH_2 rock + $\nu_{as}C-C-C$
1030vs	1035w	1035w	1030w	—	—	—	—	
—	1025s	—	—	—	—	—	—	$C-NH_2$
1015w	1010w	1000w	1015w	1020s	1020s	1020m	1015w	
—	770vw	785s	780s	—	770s	760w	—	$\nu(C-N)+\nu(N-H)$
425m	430m	450m	435m	445w	420s	445s	440w	$\nu(Ni-N)$

Table 2 indicates all mixed ligand complex show four bands in the range 1690-1500 cm^{-1} The $\nu C=C$, $\nu C=N$, $\nu(NH_2)$ and $\nu C=O$ (β-keto compound) stretches are clearly observed in all the complexes The systematic presence of C=C, C=N and C=O stretches is a necessary condition for the mixed ligand formulation[11] However, it is difficult to assign all band in the region 1690-1500 cm^{-1}, only tentative assignment of such ligand system can be given.

Direct evidence for M−O bonding could only be observed at about 440 cm^{-1} but all the M−O frequencies could not be obtained as M−O falls below the range of the instrument used.

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Synthesis and Spectral Studies of Lanthanide Complexes with Fluoro β-diketones

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LANTHANIDE β-diketonates have been found to have wide applications as pseudocontact nmr shift reagents[1-3]. Some of these chelates have been used for the chromatographic separation of lanthanides[4-5]. The paper describes the synthesis of anhydrous chelates of lanthanides with trifluoro, hexafluoro acetyl-acetone, benzoyl trifluoroacetone and pentafluoro benzoyl acetone and characterization of these by magnetic and spectral studies.

Experimental

Diaquo *tris* chelates of lanthanides with these

fluoro β-diketones have been prepared by the method described earlier[6].

Preparation of anhydrous chelates: Anhydrous chelates have been prepared by the azeotropic removal of water from the hydrated analogue. The hydrated chelate was refluxed with benzene containing ethanol under a highly efficient fractionating column. The ternary azeotrope consisting of water-benzene-alcohol was fractionated out at a high reflux ratio (~30 : 1). The amount of water collected in the distillate was estimated. The anhydrous chelate was obtained after removal of solvent under reduced pressure. The product was later purified by recrystallization from refluxing benzene.

Infrared spectra in KBr pellets were recorded on Perkin Elmer 521 spectrophotometer. Absorption spectra of the benzene solution of the chelates have been recorded on Carl Zeiss double beam spectrophotometer.

Lanthanides were estimated by first decomposing the chelate by concentrated nitric acid and evaporating it to dryness. The dried mass was extracted with dil. HCl and the metal was precipitated as oxalate by addition of excess ammonium oxalate.

The analytical data are summarised in Table 1.

TABLE 1—ANALYTICAL DATA

Sl No	Complex	%M Found	%M Calcd	%C Found	%C Calcd	Mol wt Ebulio	Mol wt Cryosco.
1	$Pr(TFAA)_3$	23.6	23.47	30.2	30.02	1080	1300
2	$Nd(TFAA)_3$	24.0	23.90	30.2	29.85	(1.8)	(2.16)
3	$Sm(TFAA)_3$	24.8	24.65	29.8	29.55		
4	$Ho(TFAA)_3$	26.6	26.42	29.0	28.86		
5.	$Er(TFAA)_3$	26.8	26.69	29.0	28.75		
6.	$Pr(HFAA)_3$	19.5	18.83	24.8	24.21	1250	1600
7	$Nd(HFAA)_3$	19.5	19.30	24.3	24.10	(1.75)	(2.2)
8	$Sm(HFAA)_3$	20.1	19.95	24.1	23.91		
9	$Ho(HFAA)_3$	21.5	21.49	23.6	23.45		
10	$Er(HFAA)_3$	21.9	21.71	23.5	23.38		
11	$Pr(BZTFA)_3$	17.7	17.91	45.6	45.82	1400	1800
12	$Nd(BZTFA)_3$	18.1	18.24	45.4	45.57	(1.75)	(2.25)
13	$Sm(BZTFA)_3$	18.7	18.86	45.0	45.24		
14	$Ho(BZTFA)_3$	20.2	20.32	44.3	44.41		
15	$Er(BZTFA)_3$	20.4	20.54	44.1	44.28		
16	$Pr(PFBZA)_3$	14.1	14.04	36.1	35.91		
17	$Nd(PFBZA)_3$	14.5	14.35	35.9	35.79		
18	$Sm(PFBZA)_3$	15.0	14.85	35.7	35.57		
19	$Ho(PFBZA)_3$	16.5	16.65	35.2	35.07		
20	$Er(PFBZA)_3$	16.2	16.24	35.3	34.99		

Results and Discussion

Molecular weight determination of these chelates by cryoscopic method in benzene indicated them to be dimeric (2 to 2.2). But ebullioscopic method in refluxing benzene have shown them to have lower complexity around 1.8. The lower complexity of the chelates in refluxing benzene may most probably be due to partial ionization of the chelate in refluxing benzene.

The introduction of fluorine in the diketone pushes the C–O and C–C stretching to higher region[7]. The most intense band in these chelates is the C–O band occurring around 1610-1630 cm^{-1} region while C–C band occurs as the second intense band between 1520-38 cm^{-1} region. Both these bands have been found to shift at lower frequency as compared to the ligand. Bands occurring in the region 1200-600 cm^{-1} are due to intermixing and overlapping of bands and hence difficult to assign.

The metal ligand vibrations appear below 500 cm^{-1} while the region below 500 cm^{-1} is clear in the ligand. This region provides information on the strength of M–O bond and hence gives an idea of the comparative stability of the complexes[8]. Three bands in each of these chelates in the 410-434, 375-385, 275-295 region have been observed. The comparison of force constants (Table 2) of the three (M–O) bands indicated that the strength of M–O bond increases with the increase in the fluorine substitution. Comparing the force constants of the (M–O) band in the chelates of the same ligand, it was observed that the strength of the M–O bond increases with the atomic number of lanthanide.

Absorption: Absorption spectra of lanthanides have been a subject of several investigations[9-11]. The presence of electrons in the '4f' orbital may invoke some electron delocalization from the metal to the antibonding molecular orbital of the ligand. Karraker[12] showed that the symmetry coordination number of lanthanide ion could be predicted from the shape, intensity and wavelength of the hypersensitive transition in the visible region. The shape of hypersensitive transition of $Nd(TFAA)_3.2H_2O$ and $Nd(HFAA)_3.2H_2O$ in benzene solution was quite similar to the octacoordinated species. The similarity among the spectra indicated that in solution atleast, the dihydrated *tris* chelates have octacoordinated stereochemistry. It is of course risky to transfer conclusions from the solution measurements to the solid compounds, but we feel the evidence in hand suggests that these dihydrate *tris* chelates are most probably octacoordinated in solid state as well. The shape of hypersensitive transition of anhydrous neodymium chelate is different from the dihydrated analogue, indicating thereby that during dehydration the coordination sphere of neodymium ion changes.

Taking free ion as standard, ligands other than fluoride cause red shift of the band[13]. The magnitude of red shift (nephelauxetic effect) depends upon the change in the interelectronic repulsion parameter. The nephelauxetic ratio (β), covalency parameter (δ)[13] and bonding parameter $(b^{\frac{1}{2}})$[13] of these chelates have been calculated from the electronic spectra and the results are summarized in Table 2. The positive values of covalency parameter and bonding parameter suggest the incidence of some covalent character in the metal ligand bond. The absolute values of these parameters are

TABLE 2—IR AND ABSORPTION SPECTRAL DATA

Sl. No.	Complex	νM–O I	νM–O II	νM–O III	Average β	Average δ	Average $b^{\frac{1}{2}}$
1.	$Pr(TFAA)_3$	412(ms)	375(m)	275(w)	0.9960	0 401	0.044
2.	$Nd(TFAA)_3$	412(ms)	375(m)	277(w)	0 9956	0.467	0 047
3.	$Sm(TFAA)_3$	414(m)	276(m)	277(w)	0 9949	0 512	0 050
4.	$Ho(TFAA)_3$	415(m)	378(m)	277(w)	0 9917	0 836	0 064
5	$Er(TFAA)_3$	417(m)	380(m)	278(w)	0 9896	1 050	0 072
6	$Pr(HFAA)_3$	418(ms)	379(m)	280(w)	0 99-8	0.629	0 055
7	$Nd(HFAA)_3$	420(ms)	383(m)	280(w)	0 9953	0 472	0 019
8.	$Sm(HFAA)_3$	420(ms)	383(m)	281(w)	0 9946	0 543	0 052
9.	$Ho(HFAA)_3$	420 ms)	384(m)	282(w)	0 9905	0 959	0.068
10.	$Er(HFAA)_3$	423(ms)	385(m)	284(w)	0 9987	1 142	0 075
11	$Pr(BZTFA)_3$	416(ms)	377(m)	278(w)	0 9937	0 634	0.055
12	$Nd(BZTFA)_3$	416(ms)	378(m)	279(w)	0 9949	0 513	0 050
13	$Sm(BZTFA)_3$	418(ms)	380(m)	280(w)	0 9934	0 553	0 057
14	$Ho(BZTFA)_3$	419(ms)	382(m)	281(w)	0 9913	0 877	0 066
15	$Er(BZTFA)_3$	422(ms)	382(ms)	285(w)	0 9900	1 010	0 070
16	$Pr(PFBZA)_3$	422(ms)	378(m)	279(w)	0 9953	0 472	0 019
17	$Nd(PFBZA)_3$	422(m)	380(m)	282(w)	0 9936	0 644	0 056
18	$Sm(PFBZA)_3$	424(m)	380(m)	283(w)	0 9914	0 563	0 053
19	$Ho(PFBZA)_3$	426(m)	382(m)	285(w)	0 9893	1 080	0 073
20	$Er(PFBZA)_3$	428(m)	384(m)	287(w)	0 9873	1 286	0 080

of little significance, yet these values are useful in a comparative study of the bonding in these complexes

These anhydrous complexes have been found to dissolve in organic solvents. The molar conductance of these chelates in benzene ranges between 3.2-5.8 mho and in DMF 10 0-12.0 mho suggesting that they behave almost like non-electrolyte The low degree of dissociation suggests that these are of inner sphere complexes

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Polyamino Chelates of Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) using Cysteine as a Secondary Ligand

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A large number of studies on the interaction of transition metal ions with amino acids have been carried out because of their biological interest[1-5] They have also been studied in relation to the determination of their structure and formation constants using various physico-chemical methods These information on the simple metal complexes of cysteine[6-11] are also available but a very little has been done on the mixed ligand complexes of this reagent[12-14] The present investigation on ternary complexing system of bivalent metal ions involving dipyridyl and *o*-phenanthroline as primary and cysteine as secondary ligand, is an attempt to fill this gap.

Irving and Rossotti *p*H-titration technique[15] as modified by Chidambaram and Bhattacharya[16] has been used for the determination of stability constants. All the experiments were carried out at 24±1° and at μ=0.1M ($NaClO_4$) in aqueous

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medium. The titration curves for Ni(II)-dipy-cysteine system are given in Fig. 1. In other systems also, the nature of the curves were the same.

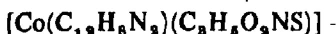
Solutions and related materials: All the solutions were prepared in doubly distilled CO_2 free water and the reagents used were of analytical grade. Solutions of metal chlorides (0.01*M*), perchloric acid (0.002*M*) and sodium perchlorate (1.0*M*) in double distilled water and of palladium chloride (0 01*M*) in 0.1*M* HCl were prepared and standardised. Solutions of the ligands were prepared by direct weighing.

Apparatus As reported earlier[17], electronic spectra were recorded using CZ-SPECORD-UV-VIS recording spectrophotometer.

Preparation of the complexes: The solutions (0.02*M*) of metal ion, amine (dipyridyl or phenanthroline) and cysteine were mixed in the ratio of 1 : 1 . 1 and then refluxed for half an hour on a water bath. The mixture was then allowed to cool in an ice bath for about 24 hr. The crystals formed were filtered, washed several times with 50% methanol to make the complexes free from reactants, dried in a desiccator over anhydrous sulfuric acid and then analysed for the metal, carbon and hydrogen.


$[Co(C_{10}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. Co, 17.64 ; C, 46 71 ; H, 3 89%

Found . Co, 17 48 ; C, 46.24 , H, 3.86%.


$[Co(C_{12}H_8N_2)(C_3H_6O_2NS)]$ -
Calcd. . Co, 16.46 ; C, 50 28 ; H, 3 63%.

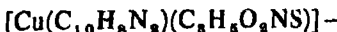
Found Co, 16 31 ; C, 49.78 , H, 3.59%.


$[Ni(C_{10}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. . Ni, 17.59 , C, 46 74 , H, 3.89%.

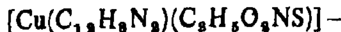
Found . Ni, 17.50 ; C, 46.23 ; H, 3 84%.


$[Ni(C_{12}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. . Ni, 16 41 ; C, 50.32 , H, 3.63%.

Found . Ni, 16.31 ; C, 50.81 ; H, 3 60%.


$[Cu(C_{10}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. · Cu, 18.77 ; C, 46 07 , H, 3.83%.

Found Cu, 18.67 , C, 45.56 ; H, 3.80%


$[Cu(C_{12}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. : Cu, 17.52 ; C, 49 64 ; H, 3.58%.

Found . Cu, 17.44 ; C, 49.09 , H, 3.53%.


$[Zn(C_{10}H_8N_2)(C_3H_6O_2NS)$ –
Calcd. : Zn, 19.20 ; C, 45.83 , H, 3.81%.

Found . Zn, 19.05 ; C, 45.39 ; H, 3.79%.


$[Zn(C_{12}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. : Zn, 17.94 ; C, 49.40 , H, 3.56%

Found . Zn, 17.76 ; C, 48.88 ; H, 3.53%.


$[Pd(C_{10}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. : Pd, 27.89 ; C, 40.90 ; H, 3.40%

Found : Pd, 27.62 ; C, 40.55 ; H, 3.38%.


$[Pd(C_{12}H_8N_2)(C_3H_6O_2NS)]$ –
Calcd. : Pd, 26.24 ; C, 44.40 ; H, 3.20%.

Found . Pd, 25.92 ; C, 43.95 ; H, 3.16%.

All the complexes were non-electrolytic in 50% alcohol.

Results and Discussion

Titration curves for Ni-(DPY)-cys system are given in Fig. 1. Similar curves were obtained in the case of the other systems. 1 : 1 (Ni – DPY) complex is formed at $pH \approx 4.0$ which remains stable up to $pH \approx 8.5$ after which hydroxo complexes $M(DPY)(OH)_n$ are formed. Beyond $pH \approx 9.0$, the complexes

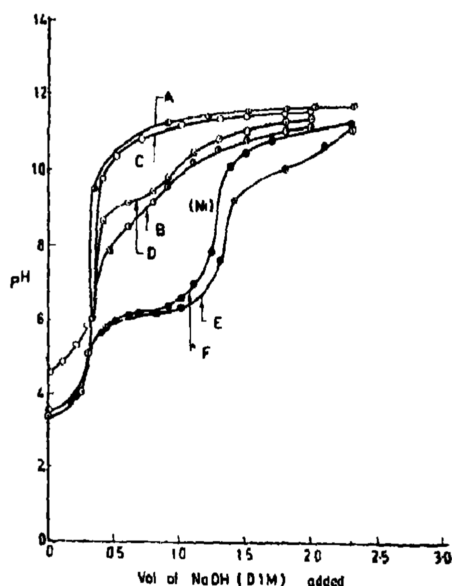


Fig. 1. Curve A—25 ml $HClO_4$ (0 002*M*)
B—20 ml $HClO_4$ (0 002*M*) + 5 ml Cysteine (0 01*M*) in 0 002*M* $HClO_4$
C—Mixture A+5 ml Dipyridyl (0 01*M*)
D—Mixture C+5 ml Nickel Chloride (0 01*M*)
E—Mixture B+5 ml Nickel Chloride (0 01*M*)
F—Mixture E+5 ml Dipyridyl (0.01*M*)
Total volume made up=50 ml (μ=0 1)

are decomposed to form the metal hydroxides which ultimately precipitate out Mixed ligand titration curve departs from the curves of cysteine at a $pH \approx 5.5$ i.e., above the formation of 1 : 1 (Ni – DPY) species and below the $pH \approx 8.5$ at which the hydroxo complex is formed. Further, in the titration curve of Ni – DPY, the precipitates were formed at $pH \approx 9.2$ while no precipitation was observed in the mixture F at this *p*H. This indicates that mixed ligand complexation has occurred. In the case of copper(II), a purple black colour appeared on mixing the solution of copper(II) and cysteine, faded and the solution then became turbid. This confirmed the observation of previous workers[18,19] that copper(II) complexes of cysteine are highly unstable. But in presence of dipyridyl or *o*-phenanthroline such type of changes were not observed and the bluish green colour formed on

mixing the reactants remained stable during the course of the titration, and the formation of precipitates were observed only beyond $pH = 9.4$.

The dissociation constants, pK_1 and pK_2 of cysteine at 24° were 8.05 and 10.30 respectively These are in good agreement with the published values[20,21]. The formation constants of the mixed ligand chelates are given in Table 1. The value of $\log K^{M-DPY}_{M-DPY-Cys}$ and $\log K^{M-Phe}_{M-Phe-Cys}$ of the metal complexes is less than the corresponding values for metal-cysteine ($\log K_1$) complexes because of statistical factors. In binary systems cysteine coordinates to the metal through amino and sulphydryl group[10] but in ternary systems as in our case, coordination seems to occur through amino and carboxylate ion as indicated by the lower values of stability constants. Such a lower value is also reported in the case of metal alanine complex ($\log K_1 = 5.94$) where also, the coordination occurs through amine and carboxylate ion[2]

TABLE 1—FORMATION CONSTANTS OF MIXED LIGAND CHELATES AT 24° ($\mu = 0.1M$, $NaClO_4$)

Metal	$\log K^{M-DPY}_{M-DPY-Cys}$	$\log K^{M-Phe}_{M-Phe-Cys}$	$\log K_1^*$ (M-Cys)
Co(II)	4 45	4 30	9 30
Ni(II)	5 55	5 45	9 64
Cu(II)	6 00	5 90	Unstable
Zn(II)	5 35	5 05	9 86
Pd(II)	5 60	5 45	—

* Literature value

The presence of a strong band at 3400 cm^{-1} and the shifting of a band from 1700 cm^{-1} (cysteine) to ≈ 1600 cm^{-1} (in complexes) in the ir spectra of complexes also indicated the coordination of the secondary ligand through amine and carboxylic group.

The electronic spectra of solutions of diamagnetic Ni(II) complexes in 50% ethanol gave five bands at 41000, 33500, 32500, 31000 and 26500 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1E_u$, $^1A_{1g} \rightarrow {}^1A_{2u}$, $^1A_{1g} \rightarrow {}^1B_{1u}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively. Similarly, the solutions of diamagnetic Pd(II) complexes gave the bands at 38000, 30000, 28500 and 22500 cm^{-1} corresponding to the $^1A_{1g} \rightarrow {}^1B_u$, $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively The observed magnetic moment value 1.85 B.M. of Cu(II) complexes was very close to that predicted for spin only value Three bands at 21500, 20000 and 16000 cm^{-1} were observed corresponding to the transitions, charge transfer, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ respectively. Thus the complexes of Ni(II), Pd(II) and Cu(II) were found of square planer structure. In the case of Co(II) complexes, the value of magnetic moment was found to be 4.50 B M. which is usally encountered in tetrahedral cobalt(II) complexes[22]. Secondly, their electronic spectra gave the bands at 25000 and 32500 cm^{-1} which correspond to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ respectively.

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Infrared Spectra of Some New Dithiocarbamates

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and

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THE present communication describes synthesis and infrared spectra of a new series of dithiocarbamates, $(C_6H_5CH_2)(R)NCS_2^-$, viz ,

$R = H$, benzyldithiocarbamate ($BzHNCS_2^-$),

$R = CH_3$, benzylmethyldithiocarbamate ($BzMeNCS_2^-$),

$R = C_2H_5$, benzylethyldithiocarbamate ($BzEtNCS_2^-$),

$R = C_3H^i_7$, benzylisopropyldithiocarbamate ($BziPrNCS_2^-$),

and $R = C_6H_5CH_2$, dibenzyldithiocarbamate ($Bz_2NCS_2^-$).

Variation in ν(CN) with the change in R group has been discussed. A comparison has also been

TABLE 1—ANALYTICAL DATA AND IMPORTANT INFRARED BANDS (cm^{-1})

Compound	m p °C	C% Found (Calcd.)	H% Found (Calcd)	N% Found (Calcd.)	$\nu_{(C-N)}$	$\nu_{(CSS)asy}$	$\nu_{(CSS)sym}$
1. $BzHNCS_2NH_4$	126	47.91 (48 00)	5.88 (6 00)	14 30 (14.00)	1361 s	920 vs	684 vs
2 $Bz_2NCS_2K\ 3H_2O$	101	49.27 (49.32)	5.51 (5.48)	3.73 (3 84)	1442 vs	972 vs 990 vs	700 vs
3 $BzMeNCS_2Na\ 3H_2O$	250-252	39.39 (39.57)	5.80 (5 86)	5 09 (5 13)	1470 s	952 vs 972 vs	700 vs
4 $BzEtNCS_2NH_4$	113	52.69 (52 69)	7 39 (7 02)	12 19 (12.28)	1447 s	958 s 940 vs	690 vs
5 $BziPrNCS_2Na.3H_2O$	68-70	43 77 (43 85)	6 71 (6 64)	4.53 (4 65)	1432 vs	962 vs	694 s
6 Me_2NCS_2Na (Ref 3)	—	—	—	—	1503 s		
7 Et_2NCS_2Na (Ref. 3)	—	—	—	—	1477 s		
8. $PhHNCS_2NH_4$ (Ref 4)	—	—	—	—	1325 s		

made with ν(CN) values for dialkyldithiocarbamates and phenyldithiocarbamate.

Preparations of the dithiocarbamates The amines used for the preparation of dithiocarbamates were obtained from Aldrich Chemical Co , Dorset, and were used as received The dithiocarbamates were prepared as the sodium, potassium or ammonium salts as described below.

(i) *Ammonium benzyldithiocarbamate* ($BzHNCS_2$-NH_4) Benzylamine (0.1 mole) was slowly run in 15 min with vigorous stirring into an ice cooled solution containing CS_2 (0.1 mole) and concentrated ammonia (sp gr. 0 89 , 0 1 mole) maintaining the temperature of the reaction mixture between 0-5° A white crystalline product was obtained, which was washed first with a little cold water, then several times with solvent ether and finally suction dried. The product was recrystallised from acetone-chloroform mixture. Yield, 70%.

(ii) *Potassium dibenzyldithiocarbamate trihydrate* ($Bz_2NCS_2K.3H_2O$),

(iii) *Sodium benzylmethyldithiocarbamate trihydrate* ($BzMeNCS_2Na.3H_2O$),

(iv) *Ammonium benzylethyldithiocarbamate* ($BzEtNCS_2NH_4$),

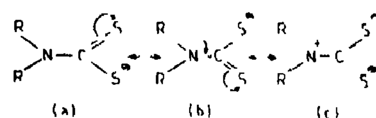
(v) *Sodium benzylisopropyldithiocarbamate trihydrate* ($BziPrNCS_2Na.3H_2O$) ·

An aqueous solution containing 0.1 mole each of the base ($NaOH/KOH/NH_4OH$) and the amine dissolved in minimum amount of water was cooled to 15° in ice cooled water (to 0° in an ice bath in the case of benzylmethyl amine). To this cooled solution 0.1 mole of CS_2 was added dropwise with stirring. After about half an hour the whole mass solidified. The white solid mass was dried in air and dissolved in minimum quantity of pure acetone. An excess of carbon tetrachloride was added to this solution when a shining white compound separated out. It was filtered and suction dried. The product was recrystallised from acetone-chloroform mixture. Yield, 70-75%.

Analytical data alongwith other physical characteristics of the dithiocarbamates are given in Table 1.

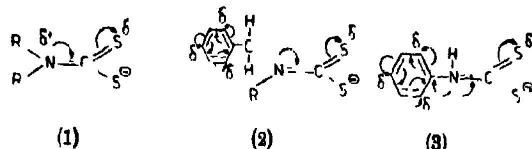
Infrared spectra : The infrared spectra of the dithiocarbamates were recorded in KBr pellets on a Perkin Elmer 621 recording spectrophotometer in the range 4000-200 cm^{-1} as well as on Perkin Elmer 137 infracord spectrometer in the range 4000-700 cm^{-1}. Important infrared spectral bands are given in Table 1. $\nu_{(CN)}$ for Me_2NCS_2Na, Et_2NCS_2Na and $PhHNCS_2NH_4$ are also given for the sake of comparison.

The structure of the dithiocarbamate anion can be represented by the following resonating forms :



The extent to which the resonance form (c) contributes to the overall dithiocarbamate structure determines the extent of double bond character of the (C–N) bond[3].

A perusal of the data in Table 1 reveals that CN stretching frequencies for the present dithiocarbamates are slightly lower than those for dialkyldithiocarbamates and much higher than those of phenyldithiocarbamate This observation may be explained on the basis of the electronic effects shown below :



In dialkyl dithiocarbamates (1) R groups release electrons through +I inductive effect and the lone pair on the nitrogen atom becomes more available for the formation of double bond. In aryldithiocarbamates (3), on the other hand, there is a very large reduction in the double bond character of the (CN) bond due to electron withdrawing effect on the phenyl ring. In the present dithiocarbamates (2), although $-CH_2-$ of the benzyl group releases electrons through hyperconjugation into the

π-electron system of the phenyl ring, the overall -I inductive effect of the benzyl group is not significant as in the case of phenyl group, because the latter is directly attached to the nitrogen atom carrying a lone pair of electrons. Thus, the double bond character in case of these ligands would be higher than in the phenyldithiocarbamates and lower than in the dialkyldithiocarbamates.

Also, the (CN) bond order in the present dithiocarbamates is $BzMeNCS_2 > BzEtNCS_2 > Bz_2NCS_2 > Bz\text{-}iPrNCS_2 > BzHNCS_2$. The Bz group being common, the order can be explained on the basis of electronic effects of the other group, viz. H, Bz, Me, Et and *iso*-Pr. When H of the benzyldithiocarbamate is replaced by benzyl or alkyl group, the (CN) bond order is increased due to the electron donating tendency of the alkyl groups. If the electronic effects were purely inductive in nature, the (CN) bond order should increase as the size of the alkyl group increases. But in case of BzMedtc, BzEtdtc and Bz*iso*-Prdtc a reverse trend is observed i.e the (CN) bond order decreases as we proceed from methyl to isopropyl through ethyl. In the dithiocarbamates, as the alkyl groups are attached to the partially double bond nitrogen, hyperconjugation is expected to be operative and the electron releasing ability can be in the order Me > Et > *iso*-Pr. The position of Bz_2dtc can similarly be explained. However, kinematic effects due to increasing mass of the alkyl group have also been suggested to be responsible[5,6].

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Stability Constants of Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) Complexes of 2, 2'-Dipyridyl-2-Pyrimidylhydrazone

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2, 2'-Dipyridyl-2-pyrimidylhydrazone (DPPmH) was employed by Singh[1] for spectrophotometric determination of various transition metals. In this paper the stepwise stability constants of binary complexes of DPPmH at *p*H 9.0 are reported. At *p*H 9.0 these metals are simultaneously determinable[2,3] and hence *p*H 9.0 is selected for present studies. The Yatsimirskii's[4,5] and Lenden's[6] graphical extrapolation methods were applied with necessary modification[7] to calculate the values of stepwise stability constants. The experiments were performed at constant temperature 30±1°.

Experimental

2, 2'-Dipyridyl-2-pyrimidylhydrazone (DPPmH) was prepared as described earlier[1]. 0 002*M* reagent solution in 40% ethanol-water was used. Solutions of Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) were prepared and standardised as reported in earlier communications[2,3]. 1 0% Ascorbic acid in distilled water was used to prevent oxidation of Fe(II)

Apparatus : Beckman model DU 2 spectrophotometer with quartz cells of 10 mm light path was used for all photometric measurements. An ELICO *p*H-meter with glass and saturated calomel electrodes was employed for *p*H adjustments. All measurements were made at 30±1° using thermostat.

Procedure A solution containing a known quantity of metal ion [Fe(II) = $3.0\times10^{-5}M$, Co(II) = $2.0\times10^{-5}M$; Ni(II) = $8.0\times10^{-6}M$, Cu(II) = $1.0\times10^{-5}M$ and Cd(II) = $7.5\times10^{-6}M$] varying quantity of DPPmH solution and 2 ml 1% ascorbic acid was adjusted to *p*H 9.0 in 40% ethanol-water, total volume being 25 ml. The absorbances were noted at respective wavelengths of maximum absorption [580, 460, 430 and 440 nm for Fe(II), Co(II), Ni(II), Cu(II) and Cd(II), respectively] against the reagent as a blank. The concentration of complex formed was computed from the appropriate calibration curve

TABLE 1—STABILITY CONSTANTS FOR DPPmH COMPLEXES AT *p*H 9 0

	Yatsimirskii's method	Leden's method	Mole ratio method
	Fe(II)-DPPmH		
log K_1	5.34	5.08	—
log K_2	4 95	4.40	—
log β_2	10 29	9.48	10.13
	Co(II)-DPPmH		
log K_1	4.79	4 78	—
log K_2	4 52	4.52	—
log β_2	9.31	9 30	9.84
	Ni(II)-DPPmH		
log K_1	5.67	5 70	—
log K_2	5.40	5 45	—
log β_2	11 07	11 15	11.61
	Cu(II)-DPPmH		
log K_1	5.25	5 16	—
log K_2	4 97	4 97	—
log β_2	10.22	10.13	10 88
	Cd(II)-DPPmH		
log K_1	6 26	6.30	—
log K_2	5 97	6 05	—
log β_2	12 23	12.35	12.30

Results and Discussion

The stoichiometric studies[8-10] revealed that the complexes are binary [1 . 2, M L] in nature.

Stability constants The metal-ligand stepwise stability constants at *p*H 9.0 of these complexes were computed from the spectrophotometric data by Yatsimirskii's[4,5] and Leden's[6] methods in modified forms[7].

The equilibrium constants thus obtained are reported in Table 1.

It is seen from Table 1 that the overall stability constants by these three methods agree with each other.

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The author is grateful to Prof. K. N. Munshi, Head, Department of Chemistry, Nagpur University, Nagpur for facilities and encouragement.

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Selectivity of Heterogeneous Ion-Exchange Membrane Discs with Reference to their Water Content, Porosity, Swelling, Electrolyte Absorption and Electrical Conductance

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IN heterogeneous membranes, the effect of binder cannot be ignored and so the study of some basic properties of the membrane becomes necessary. Michaelis[1] was the first to establish the standard electrochemical criteria for membrane characterisation, i.e., water content, porosity, swelling, electrolyte absorption and electrical conductivity. Later Gregor[2,3], Wyllie[4] and Hale[5] reported on the characterisation of heterogeneous ion selective membranes. Recently, we have used the heterogeneous membranes of pyridinium molybdoarsenate[6] (PMA) and rubidium[7] and copper(II)[8] tungstoarsenates (RbWA and CuWA) as ion selective electrodes. Present communication reports on the basic characteristics and its relationship with electrochemical performance of these heterogeneous ion exchanger membrane discs.

Experimental

Reagents and materials All the reagents used were of analytical grade Respective compounds, i.e., PMA, RbWA and CuWA and their heterogeneous membranes in Araldite were prepared as reported earlier[6-8]. Observations were made with two membranes of each exchanger

Water content, porosity, swelling and electrolyte absorption[2,5] · The membrane was kept immersed in a solution of 1 mol dm^{-3} NaCl for 24 hr to attain equilibrium It was then taken out and the adhering electrolyte was wiped out. The thickness of this swollen membrane and its difference with that of dry membrane was taken as swelling [An average value of the thicknesses measured carefully at different points of the membrane with a screw gauge (l.c. = 0 001 cm) was taken as the thickness of the membrane] The membrane was then washed several times with conductivity water and dried in a vacuum desiccator The washings were collected to measure electrolyte absorption, conductometrically. The dried membrane was weighed to a constant weight and the difference in this weight (Ww) and the weight (Wd) of the membrane before immersing in the electrolyte solution divided by Ww was taken as water content The porosity[10] (ϵ) was calculated from the relationship,

$$\epsilon = \frac{Ww - Wd}{A.L.\ \rho w}$$

where A = area of the membrane, L = thickness of the membrane and ρw = density of water.

Conductance The method recommended by Lakshminarayanaiah[11] was used for the determination of conductance of the membranes. The membrane was cemented between two half cells with the help of Araldite. It was then equilibrated by filling the half cells with 0.1 mol dm^{-3} NaCl solution. The solution was then replaced by mercury. The conductance was measured by connecting the Pt electrodes to the conductivity bridge.

Results and Discussion

When a heterogeneous membrane is immersed in water or electrolyte solution, water or solution may penetrate into the membrane structure occupying interstices which are present or which develop as a result of the difference between the swelling of

TABLE 1—BASIC PROPERTIES OF HETEROGENEOUS ION EXCHANGER MEMBRANE DISCS OF PYRIDINIUM MOLYBDOARSENATE, RUBIDIUM TUNGSTOARSENATE AND COPPER TUNGSTOARSENATE

Exchanger Binder%	Membrane	Thickness of wet membrane mm	Thickness of dry membrane mm	Water content as % of the weight of wet membrane	Porosity %	Swelling mm	Electrolyte absorption NaCl g^{-1} wet membrane μg	Sp. conductivity milli mhos cm^{-1}
PMA	I	1.145	1.061	7 7	11.5	0 084	32.3	4.89×10^{-4}
35%	II	1 136	1.051	7 6	11.0	0.080	31.8	4.91×10^{-4}
RbWA	I	0.860	0.712	8 5	19.1	0 148	51.0	1.00×10^{-3}
30%	II	0 874	0.722	8 7	20.2	0 152	51.6	$1 10\times10^{-3}$
CuWA	I	0.970	0 775	9 3	22.0	0.195	61 5	$4 07\times10^{-3}$
30%	II	0.980	0 785	9 2	20 0	0 200	60 8	4.10×10^{-3}

hydrophilic ion exchange resin and inert nonswelling binder (hydrophobic matrix). Gregor[12] has pointed out that in heterogeneous membranes, there must be a thin film of water (resulting from interstices occupied by water or ion solution) between the hydrophilic resin particles and the surrounding hydrophobic matrix and that there are therefore two pathways for ion and water transport · (i) through the resin granules and their point of contact—a pathway of high selectivity, low water permeability and high electrical conductance and (ii) through the liquid film—of comparatively high ohmic resistance, zero selectivity and high water permeability.

It, therefore, follows that in a membrane having low values of porosity, water content and swelling, the amount of interstices available are less as compared to one having relatively larger values. Thus, the membrane with low value of porosity and swelling is expected to transport current through exchange sites only (the first pathway of high selectivity) and should, therefore, respond selectively to a particular ion. It appears that an inverse relationship should exist between the selectivity of a membrane and its swelling properties. The order of swelling, water content and porosity data for the membranes studies is CuWA > RbWA > PMA (Table 1). Thus, the PMA membrane being the least swelled, should act as highly selective electrode whereas CuWA as least selective. Our potential studies[6-8] carried out on electrodes of these membranes do show such a behaviour and the selectivity order has been found to be PMA ≫ RbWA ≃ CuWA. Thus, our studies tend to show that an inverse relationship between swelling and selectivity for a membrane exists.

Electrolyte absorption studies of NaCl (Table 1) reveal that the amount of NaCl absorbed is maximum for CuWA membrane and minimum for PMA membrane. This is expected on the basis of porosity and swelling values of the membranes.

While recording membrane conductance, it was observed that the conductance changes slowly in the beginning and attains a constant value in about 5-7 min and thereafter remains constant. Such a behaviour points to negligible polarization on the mercury membrane faces.

The conductance values (Table 1) are found to be in the order CuWA > RbWA > PMA, which is consistent with the order of electrolyte absorption and swelling When these membranes are equilibrated with 0.1*M* NaCl solution, the interstices which are already present or formed by the swelling of the exchanger particles, retain the electrolyte solution. Obviously, the conductance would depend on swelling as well as electrolyte uptake.

For CuWA membrane, the swelling and electrolyte uptake is largest and, therefore, it shows maximum conductance. In case of RbWA the values (swelling and electrolyte uptake) lie midway and so the conductance For PMA membrane, both the values are lowest and hence the conductance.

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Determination of Sodium-*N*-Alkyl/Dialkyl Dithiocarbamates by Reaction with 2,4-Dinitrobenzenesulphenyl Chloride and Alkalimetric Determination of Ammonium-*N*-Aryl Dithiocarbamates

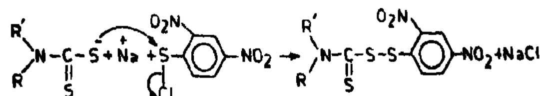
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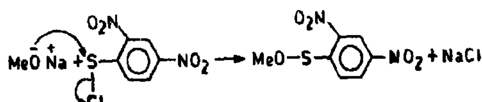
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N-SUBSTITUTED dithiocarbamates can be determined by decomposing the sample with acid followed by potentiometric titration of the excess of the latter[1]. The gravimetric method – determination of a dithiocarbamate as sulphate formed by oxidation with alkaline hydrogenperoxide[2]—is quite time consuming.

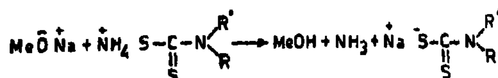
Sodium dithiocarbamates react with 2,4-dinitrobenzenesulphenyl chloride, quantitatively.



This reaction has been utilized to develop a titrimetric procedure for their determination. A dithiocarbamate is reacted with 2, 4-dinitrobenzenesulphenyl chloride in benzene-methanol, the excess of the latter is determined by titration against sodium methoxide[3], using thymol blue as indicator.



The procedure has been tested with a selection of dithiocarbamates but it seems to be applicable to others with the exception of ammonium dithiocarbamates which can, however, be titrated directly against sodium methoxide using dimethylformamide as solvent and thymol blue as indicator.



The accuracy of the procedures is evident from standard deviations recorded in Table 1.

Procedures. Sodium dithiocarbamate (30 to 100 mg, prepared and purified according to published procedures[4,5], purity checked by gravimetric determination of sulphur[2]) was dissolved in about 5 ml of methanol followed by the addition of 15 ml of benzene. 2,4-Dinitrobenzenesulphenyl chloride (DSC), in excess, was introduced. The solution was kept for 30 min before it was titrated against *ca* 0.1*N* sodium methoxide[6], using thymol

Table 1—Determination of Sodium-*N*-*Iso*butylamino Dithiocarbamate

Dithiocarbamate taken mg	DSO added mg	Titre* ml	Dithiocarbamate found mg	%Recovery
34.2	152.6	6.56	34.10	99.71
57 1	177.1	6.14	56.94	99.72
95.2	253.2	7.61	95.10	99.90

* 0.0688*M* $NaOCH_3$ used.

blue (3 drops, 0.3% in methanol) as indicator, to a distinct brown colour.

An ammonium dithiocarbamate (50 to 100 mg) was dissolved in 25 ml of dimethylformamide followed by titration against *ca* 0.1*N* sodium methoxide, using thymol blue indicator (3 drops, 0.3% in methanol), to a distinct blue colour stable for about 45 second. Complete data for the determination of one of the dithiocarbamates is given in Table 2.

Table 2—Determination of Dithiocarbamates

$$\begin{matrix} R' \\ R \end{matrix}\!\!>N-\underset{\underset{S}{\|}}{C}-\bar{S}\,\overset{+}{Na}\,(\overset{+}{NH_4})$$

No [b]	R,R'	Weight range mg	Average[a] recovery %	Standard deviation
1	Methyl, H	40-90	9 3 67(8)	0 08
2	*n*-Propyl, H	30-100	99 76(3)	0.10
3.	*iso*-Propyl, H	30-100	99.75(3)	0.05
4.	*iso*-Butyl, H	30-100	99 78(3)	0 11
5.	*P*-Oxydiethyl	30-100	99.72(3)	0.07
6.	Pentamethylene	30-100	99 76(3)	0.06
7	Phenyl, H	40-150	99.87(4)	0.06
8.	4-Ethoxyphenyl, H	50-150	99.84(3)	0 10
9	4-Chlorophenyl, H	90-100	99.87(8)	0.08

a. Figures in parentheses represent number of determination.
b. 1 to 6 are sodium salts, 7 to 9 are ammonium salts.

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Determination of Xanthates by Reaction with 2,4-Dinitrobenzenesulphenyl Chloride

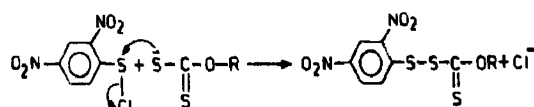
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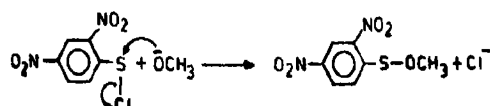
Manuscript received 18 November 1979, revised 6 July 1981, accepted 1 October 1981

ACIDIMETRIC titration in anhydrous acetic acid with perchloric acid[1] using visual or potentiometric indication, may be employed for the determination of potassium xanthates. Some xanthates can be determined by oxidation with potassium iodate[2] in alkaline medium. Iodometric determination[3] of water soluble xanthates suffers from the drawback of requiring great dilution, otherwise the fine suspension of dixanthogen leads to a false end point due to adsorption of iodine. The titration should be carried out as soon as possible because solutions of xanthates deteriorate leading to erroneous results. The gravimetric methods—determination of a xanthate as sulphate[4] formed by oxidation with alkaline hydrogen peroxide and determination as silver sulphide[5] formed by treating a xanthate with ammonical silvernitrate—are time consuming

Xanthates have been found to react with 2,4-dinitrobenzene sulphenyl chloride quantitatively.



Based on this reaction, an accurate though time consuming titrimetric procedure for their determination has been developed. A xanthate is reacted with 2,4-dinitrobenzenesulphenyl chloride in benzene-methanol, the excess of the latter is determined[6] by titration against sodium methoxide using thymol blue as indicator. The reagent is susceptible



to nucleophilic species[7]. Contamination with such species will lead to high recovery whereas acidic impurities will cause low recovery. Though tested with a selection of xanthates, the procedure seems to be applicable to others as well. Standard deviations recorded in Table 2 reveal the accuracy of the method.

Procedure : A potassium xanthate (25 to 125 mg) prepared and purified according to the published procedures[8] was dissolved in 5 ml of methanol followed by the addition of 15 ml of benzene. 2,4-Dinitrobenzenesulphenyl chloride[9] (DSC), in measured excess, was introduced. The mixture was kept for the required period of time, as mentioned in Table 2 and was titrated against $0.1N$ sodium methoxide[10], using thymol blue (3 drops, 0.3% solution in methanol) as indicator, to a green colour stable for 30 seconds. Complete details for the determination of one of the xanthates are given in Table 1.

TABLE 1—DETERMINATION OF POTASSIUM *n*-PROPYL XANTHATE

Titrant : 0.1283 *M* NaOCH$_3$, Reaction time—30 min.

Wt. of Xanthate mg	Wt. of DSC added mg	Titre ml	% Recovery
48.4	164.2	3.30	99.50
64.6	208 6	4.05	99.62
88 6	265.0	4.85	99.71
122.6	292 4	4.25	99.57

TABLE 2—RESULTS OF DETERMINATION OF SOME XANTHATES

Xanthate[a]	Weight range mg	Reaction period hr	Average% recovery	Standard deviation ±
Methyl (5)	30-130	[illegible]	99.55	0.09
Ethyl (5)	80-90	[illegible]	99.80	0.18
n-Propyl (4)	50-120	[illegible]	99.60	0.09
iso-Propyl (5)	30-100	[illegible]	99 86	0.10
n-Butyl (5)	80-125	1	99 86	0.19
iso-Butyl (6)	30-100	2	99.60	0.20
tert-Butyl (4)	40-120	1[illegible]	99 48	0 25
iso-Amyl (7)	25-100	2	99.59	0.33
Benzyl (6)	20-85	2	99.58	0.24
Cyclohexyl (4)	50-120	1[illegible]	99.40	0.15

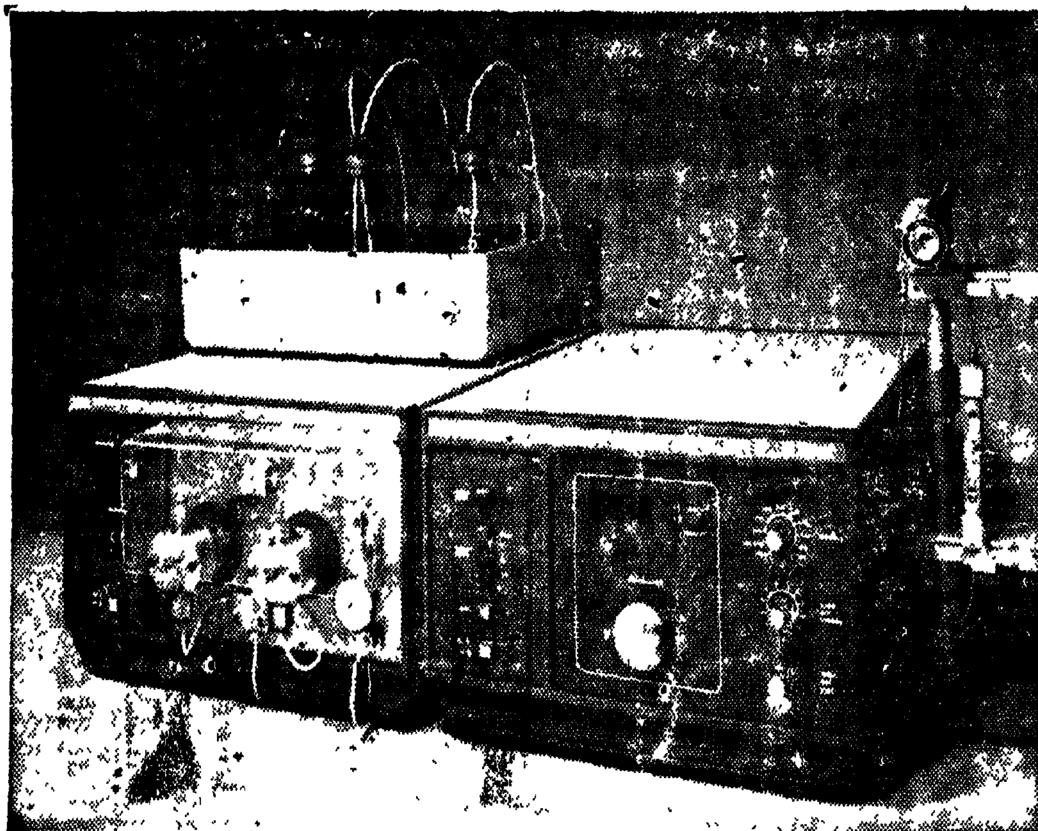
a Figures in parentheses represent number of determination.

Acknowledgement

Laboratory facilities provided by Prof. M. M. Bokadia and the award of a Junior Research Fellowship to (J. T.) by C. S. I. R. are gratefully acknowledged.

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Bis (Iodomethyl) Mercury as a CH_2 Transfer Reagent**

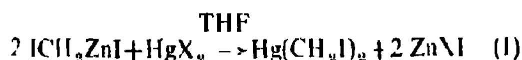
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Bis (Iodomethyl) mercury, $Hg(CH_2I)_2$, is an effective transfer agent of one CH_2 group to olefins to form cyclopropanes. Transfer of the second group (i.e., from ICH_2HgI) is not a favourable process. However, the ICH_2HgI/Ph_2Hg or the $ICH_2HgI/(PhCH_2)_2Hg$ couples serve to transfer the second CH_2 group to olefins

IN previous research we had shown *bis* (bromomethyl) mercury, $Hg(CH_2Br)_2$, to be a reasonably effective CH_2 transfer agent to olefins to give cyclopropanes[1] Bromomethylmercuric bromide and iodomethylmercuric iodide reacted similarly in the presence of stoichiometric amounts of diphenylmercury A direct CH_2 transfer from the mercurial (rather than a free CH_2 mechanism) was suggested[1] Although the yields of cyclopropanes obtained with the more nucleophilic olefins were fairly good, these reagents were not suitable for larger-scale synthetic application *Bis*(bromomethyl) mercury and bromomethylmercuric bromide were prepared by the reaction of mercuric bromide with diazomethane[2], a reagent which is both toxic and hazardous Iodomethyl mercuric iodide was prepared by the direct reaction of diiodomethane with elemental mercury and its purification was difficult[3] Neither of these reactions was suitable for rapid accumulation of larger amounts of these mercurials

It was the development of an improved route to $Hg(CH_2I)_2$ (eq 1)[4] which led us to reexamine the application of this reagent, alone and in combination with a diorganomercurial, as a CH_2 transfer agent to olefins



$$2\ ICH_2ZnI + HgX_2 \xrightarrow{THF} Hg(CH_2I)_2 + 2\ ZnXI \quad (1)$$

Experimental

Preparation of bis(iodomethyl)mercury[4] A flame-dried one-liter three-necked, round-bottomed flask equipped with a magnetic stirring assembly, a reflux condenser topped with a nitrogen inlet tube and a pressure-equalizing addition funnel was charged with 300 ml of 1 73 *M* EtZnI (0.52 mol, prepared by reaction of zinc-copper couple and iodoethane) in THF To this solution was added dropwise with stirring 152 g (0 54 mol) of diiodomethane An exothermic reaction resulted When the mixture had cooled to room temperature, a solution of 68 g (0 25 mol) of mercuric chloride in 150 ml of dry THF was added dropwise with stirring The reaction mixture was stirred at room temperature overnight, during which time a white precipitate formed Filtration provided 90 g (0 187 mol, 75%) of $Hg(CH_2I)_2$, m p 77-79° (lit[4] m p 79-81°) The product was washed several times with anhydrous diethyl ether, dried and stored in the refrigerator Recrystallization of a small portion from chloroform did not result in a higher melting point Further crops of the product, obtained from the mother liquor, were rather impure

Reaction of bis(iodomethyl)mercury with mercuric iodide Mercuric iodide, 1 0 g (2 2 mmol) and 1 2 g (2 4 mmol) of *bis*(iodomethyl)mercury were intimately mixed and heated on a steam bath until molten After 30 min of heating, most of the red colour had been discharged TLC indicated only a small spot indicative of *bis*(iodomethyl)mercury and a spot with R_f equivalent to that for authentic[3] iodomethylmercuric iodide

When the same reagents were mixed and stirred in benzene at room temperature, the dispersed colour of mercuric iodide was discharged in a few minutes, an oily solid which gradually turned yellow precipitated during this time TLC again indicated that the *bis*(iodomethyl) mercury had been consumed and iodomethylmercuric iodide had been formed

Reactions of bis(iodomethyl)mercury with olefins The reactions were carried out in flamed-out, three-necked, round bottomed flasks of appropriate size (usually 25 or 50 ml) which were equipped with a thermometer, a reflux condenser, rubber septum for sample removal by syringe, a nitrogen inlet tube and a magnetic stir-bar All reactions were carried out under an atmosphere of dry nitrogen or argon The flask was charged with the mercurial the olefin and, if any was used, the solvent in the indicated quantities (Table 1) and the resulting mixture was stirred and heated for the indicated time Aliquots (0 1-0 2 ml) were withdrawn by syringe without opening the system to air when possible In the latter stages of several reactions, clogging of the

** Dedicated, with best wishes, to Professor R C. Mehrotra on the occasion of his 60th birthday

syringe made this procedure impossible; in these cases, a disposable pipet was used. Product yields were determined by quantitative gas chromatography using appropriate internal standards. Samples were isolated by glc and their nmr and/or ir spectra were compared with those of authentic samples. Details are given in the M I T Ph.D. theses of C K H. and D D.

Reaction of bis(*iodomethyl*)*mercury with cyclooctene*: *Bis*(iodomethyl)mercury, 4.0 g (8.3 mmol), 1.00 ml (4.75 mmol) of undecane and 20 ml (154 mmol) of cyclooctene were heated to 85° for 26 hr. The red colour of mercuric iodide appeared in the reaction mixture after the first 6 hr of heating. After cooling, filtration yielded 3.45 g of a mixture of red and yellow solid with no defined melting point. The yield of bicyclo[6.1.0]nonane observed based on the transfer of one methylene group is listed below

Time	Yield
1 hr	43%
2 hr	78%
6 hr	98%
26 hr	125%

Similar descriptions of the experiments listed in Table 1 are given in the Ph.D thesis of D D

New cyclopropanes prepared in this study:

cis-*1-tert-butyl-2-methylcyclopropane*, n^{25}D 1.4128, obtained as the sole product in the reaction of $Hg(CH_2I)_2$ with *cis*-$Me_3CCH=CHCH_3$. Anal Found: C, 85.62; H, 14.37. Calcd for C_8H_{16}: C, 85.63; H, 14.37%. ^{1}H NMR (CCl_4) δ -0.20-0.70 (m, 4H, cyclopropane H), 0.95 (s, 9H, Me_3C) and 1.17 ppm (d, 3H, $CHCH_3$)

trans-*1-tert-butyl-3-methylcyclopropane*, n^{25}D 1.3982, obtained as the sole product in the reaction of $Hg(CH_2I)_2$ with *trans*-$Me_3CCH=CHCH_3$. Anal Found: C, 85.49; H, 14.38. Calcd for C_8H_{16}, C, 85.63; H, 14.37%. ^{1}H NMR (CCl_4): δ -0.20-0.50 (m, 4H, cyclopropane H), 0.80 (s, 9H, Me_3C) and 1.00 (d, 3H, $CHCH_3$)

In both cases a stereospecific reaction was observed. Although the stereochemistry of the products is not proven by experiment, it is reasonable to assume that the relative Me_3C/CH_3 geometry was retained on going from the olefin to the cyclopropane

Reaction of iodomethylmercuric iodide and diphenylmercury with cyclooctene: Iodomethylmercuric iodide, 4.7 g (10 mmol), 3.55 g (10 mmol) of diphenyl mercury, 1.00 ml (4.75 mmol) of undecane and 20 ml of cyclooctene were heated to 85° for 30 hr. Filtration of the cooled reaction mixture afforded 6.92 g (85%) of phenylmercuric iodide, m.p. 240° (lit.[9] m.p. 266°). The yield of product observed is given below:

Time	Yield
1 hr	7%
3 hr	28%
6 hr	42%
12 hr	59%
23 hr	76%
29.5 hr	78%

Reactions of bis(*iodomethyl*)*mercury, mercuric iodide and diphenylmercury with cyclooctene*: *Bis*(iodomethyl)mercury, 2.4 g (5.0 mmol), 2.3 g (5.0 mmol) of mercuric iodide, 3.55 g (10 mmol) of diphenylmercury, 1.00 ml (4.75 mmol) of undecane and 20 ml of cyclooctene were heated to 85° for 34 hr; the mercuric iodide and *bis*(iodomethyl)mercury were not pre-mixed. The cooled reaction mixture gave 7.92 g (97%) of phenylmercuric iodide, m.p. 257°. The yield of product observed at each time interval is shown below

Time	Yield
1 hr	11%
3 hr	39%
6 hr	57%
12 hr	78%
23 hr	88%
29.5 hr	93%
34 hr	93%

Reaction of bis(*iodomethyl*)*mercury and dibenzylmercury with cyclooctene*: *Bis*(iodomethyl)mercury, 2.4 g (5.0 mmol), 1.9 g (5.0 mmol, Alfa) of dibenzylmercury, 1.00 ml (4.75 mmol) of undecane and 22 ml (170 mmol) of cyclooctene were heated for 21 hr, after 5 min at 85°, the mixture had become homogeneous. The cooled reaction mixture gave 3.2 g (76%) of benzylmercuric iodide, m.p. 104° (lit.[10] m.p. 107°) upon filtration. The yield of product observed is given below

Time	Yield
1 hr	12%
2.5 hr	31%
4 hr	48%
7 hr	75%
17.5 hr	91%
21 hr	90%

Reaction of iodomethylmercuric iodide and dibenzylmercury with cyclooctene: Iodomethylmercuric iodide, 4.7 g (10 mmol), 3.8 g (10 mmol, Alfa) of dibenzylmercury, 1.00 ml (4.75 mmol) of undecane and 20 ml (154 mmol) of cyclooctene were heated for 26 hr, after 5 min of heating to 85° all of the reagents had dissolved. Filtration of the cooled mixture yielded 6.8 g (80%) of benzylmercuric iodide, m.p. 109-112°. The yield of product observed is given below

Time	Yield
1 hr	30%
2 hr	60%
4 hr	69%
6 hr	75%
26 hr	75%

Reaction of bis(*iodomethyl*)*mercury, mercuric iodide and dibenzylmercury with cyclooctene*: *Bis*(iodomethyl)mercury, 1.57 g (3.25 mmol) and 1.47 g (3.25

mmol) of mercuric iodide were stirred in 10 ml of cyclooctene for 15 min at *ca* 50° during which time most of the red colour was discharged and a small amount of an oily orange precipitate was formed To this was added 2 50 g (6 5 mmol) of dibenzylmercury, 1 00 ml (4 74 mmol) of undecane and 10 ml of cyclooctene and the reaction mixture was heated at 85° for 12 hr. All of the reagents had dissolved after heating for 5 min The cooled reaction mixture was filtered to give 3 8 g (70%) of benzylmercuric iodide, m p. 110° The yield is given below .

Time	Yield
1 hr	37%
2 hr	55%
3 hr	62%
4 hr	67%
5 5 hr	68%
8 hr	71%
11 hr	71%

Reaction of bis*(iodomethyl)mercury, mercuric iodide and dicyclohexylmercury with cyclooctene* · *Bis*(iodomethyl)mercury, 2 41 g (5 00 mmol) and 2 27 g (5 00 mmol) of mercuric iodide were heated to *ca* 50° in 10 ml of cyclooctene for 15 min Dicyclohexylmercury, 3 70 g (10 mmol), 10 ml of cyclooctene and 1 00 ml (4 75 mmol) of undecane were added and the mixture was heated to 85° for 8 hr The cooled mixture was filtered to give 7 8 g (92%) of crude cyclohexylmercuric iodide, m p 130° (lit [11] m p 142-144°). The yield is given below :

Time	Yield
1 hr	11%
2 hr	26%
3 hr	44%
5 5 hr	58%
7 5 hr	58%

A similar reaction from which no aliquots were withdrawn did not show an increase in yield.

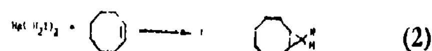
Reaction of bis*(iodomethyl)mercury, mercuric iodide, and* bis*(phenyldimethylsilylmethyl) mercury with cyclooctene* : *Bis*(iodomethyl)mercury, 2 41 g (5 0 mmol) and 2 27 g (5.0 mmol) of mercuric iodide were heated in 10 ml of cyclooctene until the red colour had been discharged. To this were added 5 0 g (10 mmol) of *bis*(phenyldimethylsilylmethyl)-mercury[12], 1.00 ml (4 75 mmol) of undecane and 5 ml of cyclooctene ; the mixture was heated at 85° for 48 hr. The yield in given below :

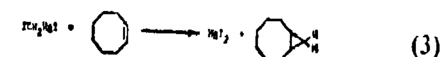
Time	Yield
3 hr	12%
7 hr	41%
19 hr	64%
22 hr	73%
25 hr	76%
34 hr	80%
48 hr	81%

Results and Discussion

Reaction of bis*(iodomethyl) mercury alone with olefins* When *bis*(iodomethyl) mercury was heated with cyclooctene in the absence of solvent at 80°, transfer of one CH_2 group per mole of reagent was complete within 6 hr (eq. 2). Transfer of the second CH_2 group occurred much more slowly under these conditions when simple magnetic stirring was used In view of this promising result, we examined $Hg(CH_2I)_2$/olefin reactions in greater detail

The progress of the CH_2 transfer process can be followed visually since the second step (eq 3) forms red mercuric iodide In practise, the reaction flask

 (2)

 (3)

was charged with 5 mmol of $Hg(CH_2I)_2$ and, usually, 10 ml of the olefin which also served as the solvent As this mixture was heated and stirred, the mercurial partly dissolved, but usually the major portion remained at the bottom of the flask as an immiscible oil The latter ranged in appearance from colourless to yellow to pale green in the various reactions As the reaction progressed, the oil gradually became more viscous and finally solidified to a white or yellow solid On continued heating, the solid phase acquired a reddish colouration which intensified until all or most of the solid present was deep red The rate at which these changes occurred could be broadly correlated, in a qualitative sense, with the reactivity of the olefin used The changes occurred in relatively quick succession with reactive olefins, but very slowly with poorly reactive ones The progress of cyclopropane product formation usually was monitored by means of quantitative gas-liquid chromatography (glc), and the reactions were stopped when no further growth of the product peak was observed, or when the solid phase in the flask was deep red In view of the difficulties in effecting rapid and complete utilization of ICH_2HgI in the second step, we report product yields in terms of eq 2=100% Thus if some utilization of ICH_2HgI occurs, yields greater than 100% will be obtained The results of our experiments are presented in Table 1

Examination of Table 1 shows that the temperature at which the reaction is carried out is an important rate-determining factor Thus, at 83° the reaction of $Hg(CH_2I)_2$ with cyclooctene gave bicyclo [6 1 0] nonane in 156% yield in a 100 hr reaction period In contrast, at 112° the reaction was much faster, giving the cyclopropane product in 120% yield within 2 hr A further temperature increase to 138° gave a 125% product yield in less than an hour Such behaviour, however, was not found with the less reactive olefins. For instance, $Hg(CH_2I)_2$ reacted with *trans*-4,4-dimethyl-2-pentene at 77° to give the expected cyclopropane in 43% yield after 7 days When the same olefin was allowed to react with this mercurial in a sealed tube at 110°, a reaction time of 8 days gave only a 44% product yield.

TABLE 1—REACTIONS OF BIS(IODOMETHYL)MERCURY WITH OLEFINS

Olefin[a] (ml)		Reaction temperature	Reaction time (days)[c]	Product (% Yield)[d]	Mercurial byproduct (% Yield)[c]	
cyclooctene	(6)[b]	25°	8	(trace)		
	(6)[b]	80°	72 hr	(148)	HgI_2	(j)
	(18)[g]	83 ± 2°	100 hr	(156)	HgI_2	(53)
	(12)	112 + 2°	2 hr	(1[illegible]0)	HgI_2	(87)
	(12)	138°	< 1 hr	(125)	HgI_2	(8[illegible])
n-$C_5H_{11}CH{=}CH_2$	(12)	94°	10	n-C_5H_{11}, H (62)	HgI_2	(78)
cyclohexene	(1 5)[e]	80 - 83°	17	(76)	HgI_2	(16)
cyclohexene	(12)	83°	52 hr	(70)	HgI_2	(38)
$AcOCH{=}CH_2$	(10)	72°	20	AcO, H (107)	ICH_2HgI	(86)
$PhCH{=}CH_2$	(4)[f]	80°	4	Ph, H (118)	HgI_2	(68)
$Me_3SiCH{=}CH_2$	(10)	55°	35	Me_3Si, H (30)	$Hg(CH_2I)_2$	(63)
cyclic olefin	(10)	(reflux)	25	(46)[h]	i	
$Me_2C{=}CMe_2$	(10)	73°	4 0	Me, Me, Me, Me (102)	HgI_2	(96)
Me_3C(H)C=C(H)Me	(9)	80°	14	Me_3C, Me, H, H (102)	HgI_2	(83)
Me_3C(H)C=C(H)Me	(9)	77°	26	Me_3C, H, H, Me (70)[h]	i	
Me_3C(H)C=C(H)Me	(6)	110 ± 5°	8	Me_3C, H, H, Me (44)[h]	i	

a Unless otherwise noted, excess olefin was used as solvent and 5 mmol of $Hg(CH_2I)_2$ were used.

b In 12 ml of benzene, 8.5 mmol of $Hg(CH_2I)_2$

c Reaction time stated is that necessary for obtaining the stated yield of cyclopropane. Actual reaction times were often much longer and were required to obtain the stated yield of mercurial byproduct, e g HgI_2

d Percentage yield is based on the amount of starting mercurial and on the transfer of one methylene (eq 2)

e In 10 5 ml benzene ; olefin/mercurial ratio = 3.

f. In 5 ml benzene, olefin/mercurial ratio = 7.

g 8.08 mmol of $Hg(CH_2I)_2$

h Not necessarily the maximum yield obtainable ; reaction stopped at this point arbitrarily.

i. Not identified.

j. Not determined.

The rate of product formation appears to depend also on the initial olefin concentration. Reactions proceeded fastest when no solvent was used and rates decreased as benzene diluent was added. However, there was no substantial effect on the final yield of cyclopropane product as solvent was added. In some cases a diluent was necessary. Thus, reaction of $Hg(CH_2I)_2$ with neat styrene at 80° resulted in extensive polymerization of the reactive olefin. In the presence of benzene diluent at 80°

TABLE 2 — COMPARATIVE REACTIONS OF $Hg(CH_2Br)_2$ AND $Hg(CH_2I)_2$ WITH OLEFINS[h]

Reaction[a]	X = Br[b,c]		X = I[d]	
	Cyclopropane yield (%)	Reaction time (days)	Cyclopropane yield (%)	Reaction time (days)
$\xrightarrow[C_6H_6,\ 80-85°]{Hg(CH_2X)_2}$	87	4 0	148	3 0
$\xrightarrow[\sim 140°]{Hg(CH_2X)_2}$	65[f]	8 hr	125	< 1 hr
$\xrightarrow[(neat\ olefin)\ 83°]{Hg(CH_2X)_2}$	67	20 hr	60 70	5 hrs 52 hr
$\xrightarrow[C_6H_6,\ 80-85°]{Hg(CH_2X)_2}$	74	8	65 76	8 17
$n\text{-}C_5H_{11}CH{=}CH_2 \xrightarrow{Hg(CH_2X)_2} n\text{-}C_5H_{11}$, H (cyclopropane)	46[f]	5 75	52[g] 62[f]	5 10
$Me_2EtCCH{=}CH_2 \xrightarrow[\sim 80°]{Hg(CH_2X)_2} Me_2EtC$, H (cyclopropane)	25	34 day	100	15 days
$PhCH{=}CH_2 \xrightarrow[\phi H,\ 80°]{Hg(CH_2X)_2} Ph$, H (cyclopropane)	22	8 days	118	4 days
$CH_2{=}CHOAc \xrightarrow{Hg(CH_2X)_2}$ OAc, H (cyclopropane)	36	23 days	107	20 days
$\xrightarrow{Hg(CH_2X)_2}$	~6	20 days	~6	25 days

a Reaction conditions denoted in this column apply to X=Br and to X=I.
b Data from reference 14
c Unless otherwise stated here or in the "Reaction" column, all reactions were carried out in benzene at 80-85°.
d Unless otherwise stated, all reactions were conducted in neat olefin at its reflux temperature
e Solvent was chlorobenzene
f Solvent was benzene/ethylbenzene, 5 : 1 by volume
g. Olefin b p 94°.
h. Cyclopropane yields are based on transfer of one XCH_2 group; yields over 100% signify additional transfer of second XCH_2 group.

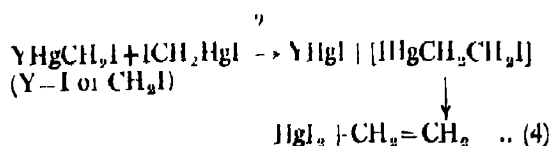
some polymerization of styrene did take place, but a reasonable yield of cyclopropylbenzene nevertheless was obtained.

The structure and the nature of the olefin also have a profound effect on the reactivity of olefins toward $Hg(CH_2I)_2$. As expected, nucleophilic olefins such as cyclooctene and tetramethylethylene underwent relatively rapid reactions to give good yields of cyclopropane product. Monosubstituted olefins such as 1-heptene and 3,3-dimethyl-1-pentene were considerably less reactive. As expected, a *cis*-1,2-dialkylethylene, *cis*-$Me_2CCH{=}CHCH_3$, was more reactive than the *trans* isomer and the reactions in each case were stereospecific.

It would be of interest to compare the reactivities of $Hg(CH_2Br)_2$ and $Hg(CH_2I)_2$ as CH_2 transfer reagents. This is not possible because different reaction conditions were used in the studies of the respective $Hg(CH_2X)_2$/olefin reactions. Nevertheless, a comparison is possible in terms of the synthetic utility of the two reagents.

The improvements of $Hg(CH_2I)_2$ over the bromomethyl-analog, as well as the unfavourable similarities, are shown in Table 2. It is clear that $Hg(CH_2I)_2$ is a more useful reagent than $Hg(CH_2Br)_2$. However, there are severe limitations on the utility of $Hg(CH_2I)_2$ and it cannot compete with the Simmons-Smith reagent, ICH_2ZnI, especially after the latter has been improved considerably[5].

There remains an unexplained discrepancy between the extent of second step CH_2 transfer (i.e., eq 3) and the yield of HgI_2 in a number of the reactions in Table 1. In analogy to the known mode of thermal decomposition of $PhHgCCl_2Br$[6], when the olefin is unreactive and/or the reaction temperature is high, CH_2 transfer into the Hg-C bond of the reagent(s) present may become competitive as suggested in eq. 4.



$$YHgCH_2I + ICH_2HgI \rightarrow YHgI + [IHgCH_2CH_2I] \quad (Y = I \text{ or } CH_2I)$$
$$\downarrow$$
$$HgI_2 + CH_2{=}CH_2 \quad (4)$$

This suggestion is speculation and has not been tested. Our ideas about the nature of the CH_2 transfer process from *bis*(halomethyl)mercury compounds to olefins also are largely speculative and have been presented in sufficient detail in our paper of the $Hg(CH_2Br)_2$/olefin reactions[1]. We remain certain that free CH_2 is not involved.

Reaction of iodomethylmercuric iodide/diorganomercurial and bis(iodomethyl)mercury/diorganomercurial systems with olefins. As mentioned above, iodomethylmercuric iodide can serve as a useful source of CH_2 when it is heated with an olefin in the presence of a stoichiometric quantity of diphenylmercury[1]. Redistribution processes to give $PhHgCH_2I$ and $Hg(CH_2I)_2$ (eq 5 and 6) occur



$$ICH_2HgI + Ph_2Hg \rightarrow PhHgCH_2I + PhHgI \quad (5)$$



$$2\,PhHgCH_2I \rightarrow Ph_2Hg + Hg(CH_2I)_2 \quad (6)$$

in this system, and it was thought possible that $PhHgCH_2I$ also is a CH_2 transfer reagent. In analogy to the known[7] $PhHgCH_2Cl$, this compound probably is quite unstable with respect to disproportionation as shown in eq 6, and it was never isolated during the course of those studies.

Our new synthesis of *bis*(iodomethyl)mercury by the organozinc route allowed us to examine in more detail the synthetic utility of iodomethylmercuric iodide as a CH_2 transfer agent to olefins. The reaction of *bis*(iodomethyl)mercury with mercuric iodide, with or without added solvent, on the steam bath provides a facile synthesis of ICH_2HgI. The conversion can be followed by noting the disappearance of the red colour of mercuric iodide. However, the prior synthesis of ICH_2HgI is not necessary, it can be prepared *in situ* by heating equimolar quantities of $Hg(CH_2I)_2$ and HgI_2 to 50° in the presence of the olefin which is to be cyclopropanated.

A comparison of the rate of bicyclo [6.1.0] nonane formation when cyclooctene and diphenylmercury are heated with authentic iodomethylmercuric iodide and with a mixture of mercuric iodide and *bis*(iodomethyl)mercury is shown in Fig. 1. It can be seen that the reaction follows the same profile in both cases. The addition of diphenylmercury has provided a means of utilizing

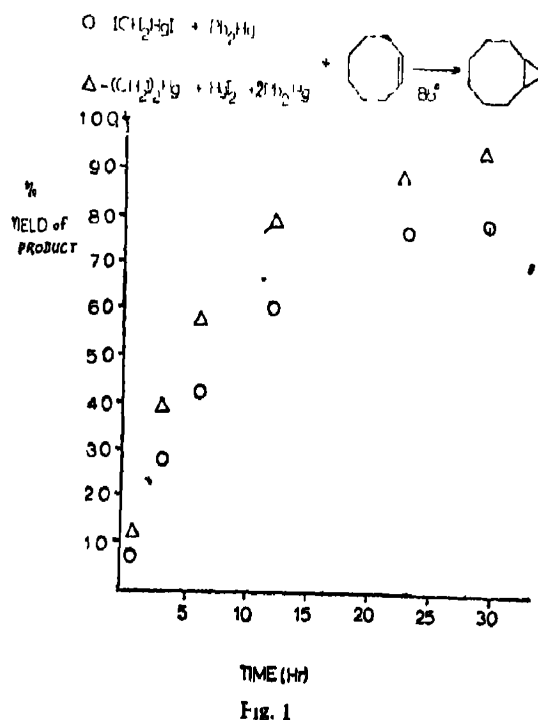


Fig. 1

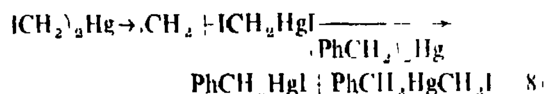
both methylene units within 30 hr of heating. Thus, in the $Hg(CH_2I)_2/HgI_2/Ph_2Hg$ system we have an effective reagent for the preparation of cyclopropanes from olefins. An extensive study of the reactivities of various olefins toward this three-mercurial reagent was not carried out, but we assume that they will parallel those found for the first ICH_2 group of $Hg(CH_2I)_2$ alone since the same basic mechanism must be involved.

At the time we were reexamining the ICH_2HgI/Ph_2Hg reagent, Scheffold and Michel[8] reported that CH_2 transfer from benzyl(iodomethyl)mercury to olefines was a more facile process than our earlier described[1] $(BrCH_2)_2Hg/Ph_2Hg$- or ICH_2HgI/Ph_2Hg-olefin reactions. However, $PhCH_2HgCH_2I$ was prepared by the reaction of $PhCH_2HgI$ with diazomethane, which, as we have pointed out in the introduction, is a toxic and potentially hazardous reagent. Accordingly, we carried out a brief study to see if an equimolar mixture of *bis*(iodomethyl)mercury and dibenzylmercury is equally effective as a CH_2 transfer reagent as $PhCH_2HgCH_2I$.

When *bis*(iodomethyl)mercury was heated with dibenzylmercury in cyclooctene at 85°, transfer of both CH_2 groups was complete within 17 hr. To determine if dibenzylmercury was undergoing redistribution with $(ICH_2)_2Hg$ (eq 7), or with ICH_2HgI formed from the loss of CH_2 from the former reagent (eq 8), dibenzylmercury was heated with



$$(ICH_2)_2Hg + (PhCH_2)_2Hg \rightarrow 2PhCH_2HgCH_2I \quad (7)$$



$$(ICH_2)_2Hg \rightarrow CH_2 + ICH_2HgI \xrightarrow{(PhCH_2)_2Hg} PhCH_2HgI + PhCH_2HgCH_2I \quad (8)$$

authentic iodomethylmercuric iodide in cyclooctene. Using this reagent system, transfer of CH_2 was complete *within 6 hr*. Thus, dibenzylmercury interacts principally with ICH_2HgI. The same results are obtained when ICH_2HgI is prepared *in situ*.

A consideration of the data from these benzyl systems indicates that, in at least this case, $RHgCH_2I$ is itself serving as a source of methylene and not merely serving as a route to *bis*(iodomethyl)mercury.

If the alkylmercurial was not itself undergoing α-elimination, then the rate of formation of bicyclo[6.1.0]nonane could not be faster in the reaction of ICH_2HgI with dibenzylmercury than for the reaction of $(ICH_2)_2Hg$ and dibenzylmercury.

When iodomethylmercuric iodide and dicyclohexylmercury were heated in cyclooctene, an increase in rate of methylene transfer was observed in comparison to that for the diphenylmercury system. However, the yield of the product observed was only 58%—an increase of only 16% over what could be obtained in the same time by using *bis*(iodomethyl)mercury alone.

Heating *bis*(phenyldimethylsilylmethyl) mercury with iodomethylmercuric iodide in cyclooctene again resulted in transfer of CH_2. In this case however, the rate of transfer was no greater than that for the phenyl-based system. Thus the observed rate of methylene transfer is dependent on the particular alkyl group used.

This brief investigation has demonstrated that *bis*(iodomethyl)mercury is the reagent of choice when an organomercury source of CH_2 is desired. It can be used directly, one methylene is transfered quickly with the reactive olefin cyclooctene. If the use of both methylene groups is desired, then conversion of $Hg(CH_2I)_2$ to ICH_2HgI with mercuric iodide and redistribution of ICH_2HgI with dibenzylmercury provide a relatively reactive reagent. All of these mercurials - ICH_2HgI, $Hg(CH_2I)_2$, $(PhCH_2)_2Hg$ and Ph_2Hg - which provide the basis for these various CH_2 transfer systems, are crystalline solids which are stable on prolonged storage. Larger quantities can be accumulated and will be ready for use when needed. Although this point was not investigated, the reactive $PhCH_2HgCH_2I$ of Scheffold and Michel should be obtainable by the reaction of ICH_2HgI with benzylmagnesium halide or benzylzinc halide.

Appendix

The reaction of bis*(iodomethyl)mercury with elemental mercury*

The 'insertion' of elemental mercury (usually a light-induced, free radical process) into C-I bonds of iodoalkanes and diiodomethane is a well-known reaction which dates back to the 1850s for the first examples[11]. The light-induced reaction of elemental mercury with diiodomethane gave both ICH_2HgI and $IHgCH_2HgI$[11]. The second product may have been formed by the reaction of the first with mercury, but it also is a product of the thermal decomposition of ICH_2HgI[3]. In view of this known chemistry, it was anticipated that the reaction of $Hg(CH_2I)_2$ might provide a route to the novel trimercurial $IHgCH_2HgCH_2HgI$. Such we found to be the case.

A mixture of 2.41 g (5.0 mmol) of $Hg(CH_2I)_2$, 2.11 g (10.6 mmol) of mercury and 15 ml of benzene was stirred at reflux under nitrogen with normal laboratory illumination for 15 hr. During the course of this time a heavy white power was formed. TLC examination of the colourless supernatant solution showed the presence of only a trace of the starting mercurial and no other soluble products. The reaction mixture was decanted from the small amount of mercury which remained and the benzene suspension of the white product thus obtained was filtered to afford 4.40 g of $IHgCH_2HgCH_2HgI$, m.p. 196-198°. The product was washed with benzene and dried at 110°. Anal. Found: C, 2.74; H, 0.59; I, 29.32. Calcd. for $C_2H_4I_2Hg$: C, 2.72; H, 0.46; I, 28.72%. ^1H NMR (dmso-d_6): δ 3.30 (s). IR (KBr pellet): 2898w, 1327broad, 959m, 633m, 600s, 560sh and 502m (cm^{-1}).

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A Highly Efficient Osmium Tetraoxide Catalyzed Oxidation of Sterically Hindered Olefins to Diols+

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The use of trimethylamine oxide as oxidizing agent in the presence of catalytic amounts of osmium tetraoxide and pyridine in refluxing aqueous *t*-butyl alcohol efficiently converts sterically hindered olefins to diols without forming the α-hydroxy ketones or other by-products encountered with previously known procedures Trisubstituted olefins with which this procedure has proved successful include α-pinene the methyl and methoxyethoxymethyl ethers of nopol, ethyl chrysanthemumate, and marginally 3-methyl-3-penten-2-one The disubstituted olefins cyclooctene and *T* 4-methyl-2-pentene were hydroxylated efficiently The new procedure also proved more efficient than *t*-butyl hydroperoxide for hydroxylation of tetramethylethylene Pyridine not only failed to enhance but substantially reduced the relatively mediocre yield of diol from α-pinene when *N*-methylmorpholine *N*-oxide was used as oxidizing agent

THE *syn*-dihydroxylation of olefins with a stoichiometric amount of osmium tetraoxide is generally efficient and useful[1], provided the product rivals gold in value Osmium tetraoxide catalyzed hydroxylations utilizing hydrogen peroxide or sodium chlorate as oxidizing agents are often practical with unhindered olefins, but tend to produce substantial amounts of α-hydroxy ketones and carbon-carbon bond cleavage products from trisubstituted olefins[1]. VanRheenen, Kelly and Cha have recently reported a particularly mild catalytic procedure with *N*-methylmorpholine *N*-oxide[2], and Sharpless and co-workers have found *t*-butyl hydroperoxide to be a useful oxidizing agent[3,4]

Our interest in this problem was prompted by the need for a chiral diol which could form boronic esters to be used in a new approach to directed chiral synthesis[5,6] α-Pinene derivatives have yielded high chiral selectivities in hydroborations[7], and cation chelation has been found to increase selectivity in directed chiral displacement reactions[8] These considerations led us to attempt the hydroxylation of nopol derivatives (1)

Experimental

Reagent grade chemicals were used Osmium tetraoxide (*TOXIC*) purchased in 1 g ampoules was dissolved in *t*-butyl alcohol to make a 2% solution, measured volumetrically 60 MHz ^{1}H nmr spectra were recorded with a Varian EM-360 instrument and 100 MHz ^{1}H nmr spectra on a JEOL MH-100 Microanalyses were by Galbraith Laboratories Knoxville, Tennessee

Nopol methoxyethoxymethyl ether (**1a**) A solution of 50 mmol of nopol in THF was treated with 60 mmol of butyllithium at 0° followed by 60 mmol of methoxyethoxymethyl chloride After 1 hr water was added and the product was extracted with ether and distilled, b p 88-90° (0 1 torr) 71%, 60 MHz nmr (CCl$_4$) δ 0 86 (s 3 C*H*$_3$) 1 19 (d *J* 8Hz 1, C*H*) 1 30 (s 3, C*H*$_3$), 2 13-2 23 (m 7 C*H* C*H*$_2$), 3 35 (s 3, OC*H*$_3$) 3 55 (m, 6, OC*H*$_2$), 4 71 (s 2, OC*H*$_2$O), 5 33 (m, 1 C C*H*) Anal Found C, 70 74, H, 10 12 Calcd for $C_{15}H_{26}O_3$ C, 70 82, H 10 31%

Nopol methoxyethoxymethyl ether diol (**2a**)

A *With stoichiometric osmium tetraoxide* A solution of 0 50 mmol of nopol MEM ether (**1a**) and 0 55 mmol of osmium tetraoxide in 2ml of pyridine was kept at 20-25° 11 hr and then treated with excess aqueous sodium bisulfite The diol (**2a**) was isolated by preparative tlc on silica gel 83%, nmr (CCl$_4$) δ 0 95 (s, 3 C*H*$_3$) 1 28 (s 3 C*H*$_3$) 1 4-2 6 (m, 8 C*H* C*H*$_2$) 3 38 (s 3 OC*H*$_3$) 3 3-4 2 (m 9, OC*H*$_2$, C*H*O*H*, O*H*) 4 71 (s 2 OC*H*$_2$O), ir (neat) 3420 (OH) Anal Found C 62 70 H 9 56 Calcd for $C_{15}H_{28}O_5$ C, 62 47, H, 9 79%

B *With t-butyl hydroperoxide* A solution of 0 50 mmol of **1a**, 0 4 mmol of 70% *t* butyl hydroperoxide and 0 35 mg of osmium tetraoxide in 2 ml of *t*-butyl alcohol was stirred 2 hr at -5 to -10° and then treated with sodium bisulfite TLC separated **2a** (42%) from less polar by-products which appeared to include substantial amounts of α-hydroxy ketone (**3a**) On a 40 mmol scale the yield of **2a** fell to 19%

C *With permanganate* A solution of 0 5 mmol of **1a** in 6 ml of *t*-butyl alcohol was added to a vigorously stirred solution of 0 73 mmol of potassium permanganate and 3 6 mmol of sodium hydroxide in 10 ml

+ Dedicated to Professor R. C Mehrotra on his 60th birthday in recognition of his contributions to Chemistry.

of water at 0°, stirred 10 min, treated with sulfur dioxide to decolorize, saturated with sodium chloride and extracted repeatedly with ether. TLC yielded 40% **2a** and substantial amounts of less polar by-products.

D. *With trimethylamine* N-*oxide* (*No pyridine*) : A solution of 1 mmol of **1a**, 1.06 mmol of trimethylamine *N*-oxide and 0 8 mg of osmium tetraoxide in 0 16 ml of *t*-butyl alcohol, 0 4 ml of acetone and 0 5 ml of water was stirred 7 days TLC analysis showed no **2a** Refluxing 30 hr followed by work-up with bisulfite and tlc yielded 27% **2a**.

E *With trimethylamine N-oxide/pyridine*. The general preparation of diols (below) was followed, 24 hr reflux, except that the **2a** was chromatographed of silica before kugelrohr distillation, bath 130-140° yielded 62% **2a**.

Attempted oxidation of nopol tosylate (**1c**) *with potassium perchlorate* Treatment of nopol with toluenesulfonyl chloride in pyridine yielded **1c**. The compound is a low-melting solid (from ether/petroleum ether) 60 MHz nmr ($CDCl_3+CCl_4$) : δ 0.80 (s, 3, CH_3), 1 10 (d, J=8 Hz, 1, CH), 1 27 (s, 3, CH_3), 2 0-2 4 (m, 7, CH, CH_2), 2 49 (s, 3, $ArCH_3$), 4.09 (t, 2, OCH_2), 5.35 (m, 1, $C{=}CH$), 7.47+7.90 (d, d, J=8Hz, 2+2) A 2 mmol sample of **1c** with 2 5 mmol of potassium perchlorate and 2 5 mg of osmium tetraoxide in 5 ml of water and 5 ml of THF after 24 hr at 20-25° showed only unchanged **1c** on tlc

Nopylmorpholine · A solution of 50 mmol of nopol tosylate and 100 mmol of morpholine in 100 ml of THF was refluxed 20 hr, concentrated, treated with water, extracted with ether, and distilled, 74%, b p 92-93° (0.05 torr), 100 MHz nmr (CCl_4) : δ 0 82 (s,3, CH_3), 1 12 (d, J=8 Hz, CH), 1 24 (s, 3, CH_3), 2 0-2 3 (m, 13, CH, CH_2, NCH_2), 3 48 (m, 4, OCH_2), 5 07 (m, 1, C-CH) Anal Found · C, 76 23, H 10.65, N, 5.70 Calcd for $C_{15}H_{25}NO$ C, 76 55, H, 10 71, N, 5.95% Attempted oxidation of this compound (0 5 mmol) with *t*-butyl hydroperoxide (0 8 mmol) and osmium tetraoxide (0 05 ml of 0 5% solution in *t*-butyl alcohol) in the presence of tetraethylammonium hydroxide (0 05 ml of 20% aq. solution) at -5 to -15° 2 hr followed by treatment with sodium bisulfite yielded a mixture of products, as shown by tlc and the presence of a strong carbonyl ir absorption at 1710 cm^{-1}.

General preparation of diols A solution of 25 mmol of the olefin, 34 mmol (3 75 g) of trimethylamine-*N*-oxide dihydrate, 1 ml of 2% osmium tetraoxide in *t*-butyl alcohol and 2 ml of pyridine in 15 ml of water and 50 ml of *t*-butlyl alcohol was refluxed 9-48 hr[17], cooled to 25°, treated with 20 ml of 20% aqueous sodium bisulfite, concentrated under vacuum to remove *t*-butyl alcohol, saturated with sodium chloride and extracted with ether (4-6 portions). Kugelrohr distillation yielded pure diol, with no by-products detectable by tlc.

Nopol methyl ether diol (**2b**) : Nopol methyl ether (**1b**)[18] was prepared by treating nopol with sodium hydride in THF followed by methyl iodide, 60 MHz nmr (CCl_4) · δ 0 84 (s, 3, CCH_3), 1 17 (d, J=8 Hz, 1, CH), 1 30 (s, 3, CCH), 2 3 (m, 7, CH, CH_2), 3 29 (s, 3, OCH_3), 3 5 (m, 2, CH_2O), 5 35 (unresolved m, 1, $C{=}CH$). The general preparation of diols, scaled up to 0 1 mol of **1b**, 17 hr reflux, kugelrohr bath 105° (0.2 torr), yielded 78% **2b** ; 60 MHz nmr (CCl_4) . δ 0.93 (s, 3, CH_3), 1.27 (s, 3, CH_3), 1 4-2.6 (m, 8, CH, CH_2), 3 39 (s, 3, OCH_3), 3 6-4.2 (m, 5, CH_2O, OH, $CHOH$) Anal Found : C, 67 05 ; H, 10 37 Calcd for $C_{12}H_{22}O_3$ · C, 67.26, H, 10.35%.

Pinanediol (5) · (+)-α-Pinene (4) in the general procedure, 0 2 mol scale, 17 hr reflux, yielded 94% **5** on simple distillation, b.p 90-91° (0 25 torr), m p 54-55.5°[19] (See large scale preparation below for further data)

cis-*Cyclooctane-1, 2-diol*. Cyclooctene, 9 hr reflux, kugelrohr bath 90° (0 4 torr), yielded 85% *cis*-cyclooctane-1,2-diol, m.p. 77-78° (lit [20] m.p. 79°)

threo-*4-Methylpentane-2, 3-diol* *E*-4-Methyl-2-pentene, 10 hr reflux, kugelrohr bath 80° (0 75 torr), yielded 78% *threo*-4-methylpentane-2,3-diol, m p 56-57 5° (lit [21] m p 59°)

Ethyl chrysanthemumate diol (7) Ethyl chrysanthemumate (6), 24 hr reflux, kugelrohr bath 100-105° (0.25 torr), yielded 91% diol 7 as an oil, nmr (CCl_4) . δ 1 2 (m, 16, CCH_3 + C_3CH), 1 93 (s, 1, $CHCO_2Et$), 3 4 (m, 3, $CHOH$ + OH), 4 17 (q, 2, CH_2O) Anal Found · C, 62 56, H, 9 59 Calcd for $C_{12}H_{22}O_4$ · C, 62 58, H, 9 63%

Pinacol · Tetramethylethylene, 23 hr reflux, simple distillation, yielded 91% pinacol contained in a mixture with ~10% pyridine by nmr analysis, redistilled, b.p 108-110° (62 torr), 83%, nmr same as authentic sample.

3-Methylpentane-2,3,-diol-4-one *E*-3-Methyl-3-penten-2-one[22] (30 mmol) was subjected to the standard conditions with 3 8 g (34 mmol) of trimethylamine oxide, modified by reducing the amount of water to 10 ml, 18 hr reflux, resulting in a black mixture (containing no unchanged enone by tlc analysis), which was concentrated and chromatographed on silica with ether before distillation, b p. 60 (0 2 torr) [lit.[23] 65° (1.5 torr)], 60 MHz nmr (CCl_4) . δ 1.13 (d, J=6 Hz, 3, $CHCH_3$), 1 15 (s, 3, CCH_3), 2.18 (s 3, $COCH_3$), 3 6 (broad s, 2, OH), 3.88 (q, 1, $CHCH_3$)

Pinanediol (**5**) (*Large scale preparation*) A mixture of 272.5 g (2 mols) of α-pinene[24], 230 g (2.07 mols) of trimethylamine oxide dihydrate, 1 g of osmium

tetraoxide, 1 5 1 of *t*-butyl alcohol, 150 ml of pyridine and 300 ml of water was refluxed gently with irring (there being a small aqueous phase present) r 4 days. After cooling, the mixture was stirred ith 20 g of sodium bisulfite 1 hr more (until the ark osmate color faded to yellow), and enough dium chloride (~60 g) was added to saturate the queous phase, which was then separated and tracted with two 100 ml portions of ether. The rganic phase was combined with the ether extracts nd concentrated under reduced pressure Pinanetol (5) was distilled rapidly at 110-116° (0 3-1.0 orr), forcing the last few grams over with the aid of heat gun, leaving only a small high-boiling sidue, solidified, yield 328 g (96.5%)[26]. TLC nalysis (ether/petroleum ether on silica gel) showed single spot; nmr ($CDCl_3$): δ 0 93 (s, 3, CH_3), 26 (s, 3, CH_3), 1.29 (s, 3, CH_3), 1.5-2.5 (m, 6, CH, CH_2), 2 9 to 3.8, dependent on concentration (broad , 2, OH), 3.93 (d of d's, J=6 and 9 Hz, $CHOH$)

Nopol MEM ether diol (phenylthio)methaneboronate : quivalent amounts of (phenylthio)methaneboronic acid and nopol MEM ether diol (2a) were refluxed 5 hr in benzene and the water separated with a Dean-Stark trap The solution was concentrated, hromatographed with ether/petroleum ether 3 7 on silica and distilled in a kugelrohr, oil, 78%, 100 MHz nmr (CCl_4) · δ 0 88 (s, 3, CH_3), 1 29 (s, 3, CH_3), 1 8-2 3 (m, 8, CH, CH_2), 2 33 (s, 2, SCH_2B), 3 39 (s, 3, OCH_3), 3 5 (m, 6, OCH_2), 4 5 (m, partially obscured, 1, O-CH), 4.55 (s, 2, OCH_2O), 7 20 (m, 5, C_6H_5). Anal Found. C, 63.07, H 8 09, B, 2 62, S, 7 86. Calcd. for $C_{22}H_{33}BO_5S$: C, 62 86; H, 7.91; B, 2.57; S, 7 63%

Nopol methyl ether diol butaneboronate: Nopol methyl ether diol (2b) and butaneboronic acid refluxed in benzene 90 min and the water separated with a Dean-Stark trap quantitatively yielded the boronic ester, b.p. 90° (0.03 torr); 60 MHz nmr (CCl_4) δ 1-2 (m, 23, aliphatic CH), 3 3 (s, 3, OCH_3), 3 45 (m, 2, OCH_2), 4.45 (m, 1, $CHOB$). Anal. Found: C, 67.95; H, 10.13; B, 3.87. Calcd. for $C_{16}H_{29}BO_3$: C, 68.58; H, 10.43; B, 3.86%.

Results

The nopol system(1)(Fig. 1) soon proved to be an especially sensitive and recalcitrant choice. Nopol methoxyethoxymethyl (MEM) ether (1a) was readily converted to the diol (2a) (83%) by a stoichiometric amount of osmium tetraoxide in pyridine[1], but the known catalytic methods were found mediocre or worse Sodium chlorate[1,9] yielded 10% 2a. *t*-Butyl hydroperoxide and tetraethylammonium hydroxide[5] yielded 19-42% 2a, accompanied by comparable amounts of less polar material presumed to be the α-hydroxy ketone (3a) as well as other by-products, separable from 2a only by chromatography. Nopylmorpholine was oxidized to a mixture including a considerable proportion of ketone (infrared evidence) with *t*-butyl hydroperoxide. Potassium perchlorate[10] failed to oxidize nopol tosylate (1c), according to tlc analysis.

Alkaline potassium permanganate[11] (no osmium) was also tested with 1a and yielded 40% 2a together with 3a and other by-products.

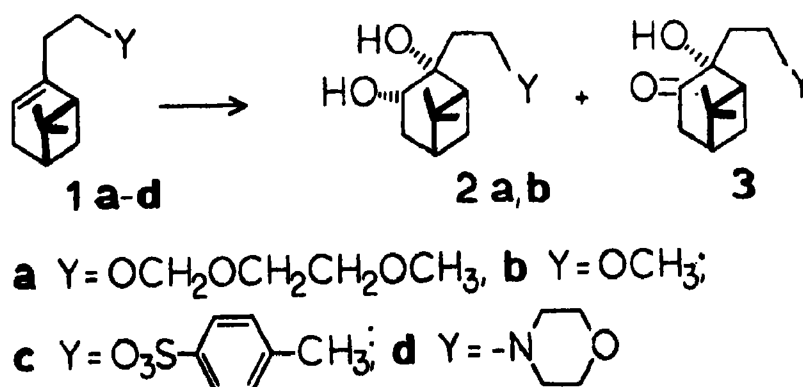


Fig 1 Oxidation of nopol derivatives.

We next tried the VanRheenen procedure[8], but with the fortunate choice of trimethylamine *N*-oxide, which happened to be immediately available, in place of the recommended[2] *N*-methylmorpholine *N*-oxide Although there was no reaction of 1a in 7 days at 25° in aqueous acetone, refluxing 30 hr converted 27% to diol 2a, significantly with no detectable α-hydroxy ketone 3a or other by-products on tlc.

Pyridine is known to promote the stoichiometric reaction of osmium tetraoxide with olefins on the basis of preparative[1,12] as well as kinetic[13] studies, and basic conditions favour hydrolysis of osmate esters[8] We therefore tried adding pyridine to our reaction mixture and on refluxing 1a in aqueous *t*-butyl alcohol 17 hr obtained 62% of diol 2a, with no by-products detectable by tlc. The yield fell to 55% after 40 hr reflux. These are among the lowest yields of the series of compounds we tested, summarized in Table 1 and may merely reflect the lability of the MEM ether group.

The diol 2a from nopol MEM ether was used to esterify (phenylthio)methaneboronic acid in the hope that the resulting boronic ester could be deprotonated at the SCH_2B group in the same manner as

TABLE 1 OLEFINS WHICH HAVE BEEN *syn*-DIHYDROXYLATED BY OsO_4/Me_3NO/PYRIDINE

Olefin	Yield of Diol, %
Nopol MEM ether (1a)	62
Nopol methyl ether (1b)	78
(+)-α-Pinene (4), (–)-α-Pinene	90-96
cis and *trans* Ethyl chrysanthemumate (6)	91
L-$CH_3CH=CHCH(CH_3)$	78
Cyclooctene	85
$(CH_3)_2C=C(CH_3)_2$	83
L-$CH_3CH=C(CH_3)COCH_3$	48

pinacol (phenylthio)methaneboronate[11] with the possibility of using the resulting anion for directed chiral syntheses. However, it appears that this methylene group is too hindered for this purpose, and several attempts gave low yields of alkylation product under the usual conditions[14], while quenching with deuterium oxide gave only partial deuteration, based on nmr spectra. As a result of these failures, the boronic ester serves merely as an exotic derivative to prove the presence of the *cis*-diol group in **2a**.

Nopol methyl ether (**1b**) yielded diol **2b**. The butaneboronic ester derivative proved inert toward dichloromethyllithium and thus could not be used for chiral synthesis by homologation[6]. These failures of boronic ester chemistry led us to abandon the series of nopol derivatives at this point in favour of a less hindered system.

The conversion of (+)-α-pinene (**4**) to (–)-pinanediol (**5**) (Fig. 2), the diol which proved useful in chiral synthesis[6], has been carried out routinely with high yields. One gram of osmium tetraoxide is sufficient to convert two moles of α-pinene. It appears that the trimethylamine evolved during the reaction may play an essential role, since inadvertent vigorous refluxing of the reaction mixture reduced the yield and produced by-products[15].

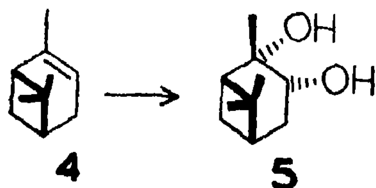


Fig. 2. Hydroxylation of (+)-α-pinene.

Unexpectedly, *N*-methylmorpholine *N*-oxide[3] proved considerably less effective than trimethylamine *N*-oxide in the oxidation of α-pinene (**4**) to pinanediol (**5**). There was no reaction after 24 hr at 25°, the "usual" conditions[3], and the yield of diol **5** after 24 hr reflux was only 63%. Pyridine not only failed to help, but lowered the yield of **5** to 36-44%, and caused formation of a substantial amount of undistillable residue. We also tested pyridine *N*-oxide with **4** but found no **5** by tlc after 24 hr reflux.

The trimethylamine *N*-oxide/pyridine/osmium tetraoxide system was tested for generality with several other olefins (Table 1). The conversion of ethyl chrysanthemumate (**6**) (*cis*/*trans* mixture) to the corresponding diol (**7**) illustrates compatibility with ester and cyclopropane functions (Fig. 3).

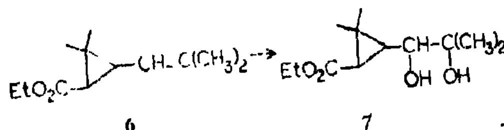


Fig. 3. Hydroxylation of ethyl chrysanthemumate.

Disubstituted olefins react smoothly, and the yield of cyclooctanediol was slightly better than that from the *N*-methylmorpholine-*N*-oxide method. A tetrasubstituted olefin, tetramethylethylene, was converted to pinacol in better yield than the previously reported 72% with *t*-butyl hydroperoxide as oxidizing agent[3]. *N*-Methylmorpholine *N*-oxide has been reported to fail with a tetrasubstituted olefin[4]. It should be noted that most of our yields are from single attempts and are not necessarily optimum.

The usual oxidation conditions proved marginally successful with an α,β-unsaturated ketone, *L*-3-methyl-3-penten-2-one, $CH_3CH=C(CH_3)COCH_3$, which yielded 48% of a single diol $CH_3CHOHCOH(CH_3)COCH_3$, after separation from tarry by-products. No detectable diol (by nmr) was formed after 39 days at 20-25° and the recovered 3-methyl-3-pentene-2-one was contaminated with a gross amount of unidentified unsaturated by-products.

Hauser and Rhee have successfully applied our method to a disubstituted olefin bearing amide and ester substituents and obtained 92% of lactonized product[16].

In summary, the osmium tetraoxide catalyzed oxidation of olefins by trimethylamine *N*-oxide in the presence of pyridine provides a convenient and efficient general method for preparing 1,2-diols.

Acknowledgement

We thank the National Science Foundation for grant no. CHE77-11283.

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24 Aldrich Chemical Co 92% enantiomeric excess (+)-isomer The (−)-isomer, 82% e e, gave similar results
25 Half the proportion of *t*-butyl alcohol has been used, with 85-90% yields resulting, doubling the proportion of osmium tetraoxide permits completion in half the time

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Reactions of Allylmetal Carbonyls of Rhodium and Cobalt with Carbon Monoxide and Hydrogen : New Catalytic Intermediates in Homogeneous Hydroformylation Reactions

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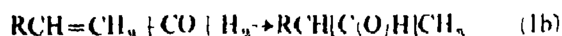
Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

Reactions of the trihaptoallyls $C_3H_5Rh(CO)_2$ and $C_3H_5Co(CO)_3$ with CO and H_2 at elevated pressures in n-tetradecane solution have been followed by infrared spectroscopy under pressure using the ν(CO) region to identify carbonyl intermediates. Thus the rhodium complex $C_3H_5Rh(CO)_2$ is carbonylated reversibly to a new $RRh(CO)_4$ derivative [either $CH_2{=}CHCH_2Rh(CO)_4$ or $CH_2{=}CHCH_2C(O)Rh(CO)_4$] which is only stable at elevated CO pressures. Hydrogenation of $C_3H_5Rh(CO)_2$ also gives a new species tentatively formulated as the propene complex $HRh(CO)_3(CH_2{=}CHCH_3)$. A related complex, possibly $HRh(CO)_3(C_2H_4)$, is generated by the reaction of $Rh_4(CO)_{12}$ with C_2H_4/H_2 mixtures in the absence of CO ; this species is an active hydroformylation catalyst under mild conditions. The cobalt complex $C_3H_5Co(CO)_3$ is carbonylated reversibly to $CH_2{=}CHCH_2Co(CO)_4$, again a species stable only under elevated CO pressures.

THE hydroformylation of olefins with carbon monoxide and hydrogen (equations 1a and 1b) is an important method for the manufacture of aldehydes[2,3,4,5]

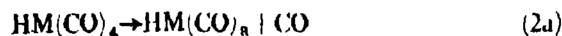


$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO \quad (1a)$$

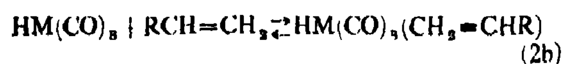


$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH[C(O)H]CH_3 \quad (1b)$$

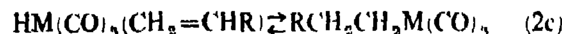
Such hydroformylation reactions are catalyzed by certain metal carbonyl derivatives including those of cobalt and rhodium. The currently accepted mechanism[6] involves the alternating production of 16- and 18-electron intermediates illustrated by the following catalytic cycle for production of terminal aldehydes according to equation 1a (for equations 2a-2h M=Co or Rh):



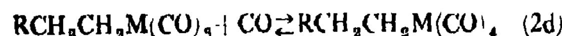
$$HM(CO)_4 \rightarrow HM(CO)_3 + CO \quad (2a)$$



$$HM(CO)_3 + RCH{=}CH_2 \rightleftarrows HM(CO)_3(CH_2{=}CHR) \quad (2b)$$



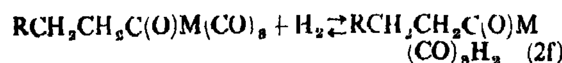
$$HM(CO)_3(CH_2{=}CHR) \rightleftarrows RCH_2CH_2M(CO)_3 \quad (2c)$$



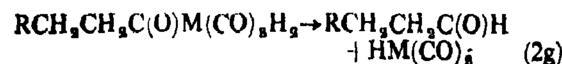
$$RCH_2CH_2M(CO)_3 + CO \rightleftarrows RCH_2CH_2M(CO)_4 \quad (2d)$$



$$RCH_2CH_2M(CO)_4 \rightleftarrows RCH_2CH_2C(O)M(CO)_3 \quad (2e)$$



$$RCH_2CH_2C(O)M(CO)_3 + H_2 \rightleftarrows RCH_2CH_2C(O)M(CO)_3H_2 \quad (2f)$$



$$RCH_2CH_2C(O)M(CO)_3H_2 \rightarrow RCH_2CH_2C(O)H + HM(CO)_3 \quad (2g)$$

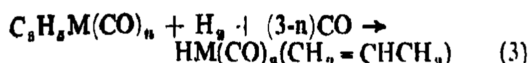


$$HM(CO)_3 + CO \rightarrow HM(CO)_4 \quad (2h)$$

Recent work from our laboratory has involved the use of infrared spectroscopy at elevated pressures to study the chemical reactivity of transition metal intermediates relevant to the above mechanism for the hydroformylation reaction. Our results in this area to date have been of the following two types : (1) study of the reactivity towards CO and H_2 of stable compounds modelling unstable reaction intermediates (e.g. metal alkyls)[6], (2) identification, by their ν(CO) frequencies, of intermediates in the above catalytic cycle which are stable only under elevated pressures [e.g. $RRh(CO)_4$ derivatives][7].

This paper describes further results relevant to the identification of unstable intermediates in the rhodium-catalyzed hydroformylation of olefins. The intermediates in the catalytic cycle 2a-2h (M=Rh) most amenable to identification are the coordinately saturated 18-electron intermediates, namely $HRh(CO)_4$, $HRh(CO)_3(CH{=}CHR)$, $RCH_2CH_2Rh(CO)_4$ and $RCH_2CH_2C(O)Rh(CO)_3H_2$. A recent elegant study[8] by Vidal and Walker using infrared spectroscopy at pressures in excess of 1000 atmospheres provides conclusive evidence for the existence of $HRh(CO)_4$ under these extreme conditions. Our previous paper noted above[7] presents infrared spectroscopic evidence for the formation of an unstable $CH_3CH_2Rh(CO)_4$ by treatment of suitable rhodium(I) derivatives with $CO/C_2H_4/H_2$ gas mixtures. This paper discusses evidence for another of the above catalytic intermediates, namely $HRh(CO)_3(CH_2{=}CHR)$. The role of trihaptoallyl derivatives in this chemistry relates to the possibility of their hydrogenation to the propylene complexes $HM(CO)_3(CH_2{=}CHCH_3)$

according to the following general scheme (M=Co, n=3, M=Rh, n=2):



$$C_3H_5M(CO)_n + H_2 + (3-n)CO \rightarrow HM(CO)_4(CH_2=CHCH_3) \quad (3)$$

However, we were led to investigate such hydrogenations of trihaptoallyl metal carbonyls only after detecting preliminary evidence for $HRh(CO)_3(C_2H_4)$ in the reaction of $Rh_4(CO)_{12}$ with C_2H_4/H_2 mixtures in the absence of CO

$Rh_4(CO)_{12}$ as a hydroformylation catalyst

Our studies in the high pressure infrared cell on the hydroformylation of ethylene by various rhodium complexes using a 1 : 1 : 1 $CO/C_2H_4/H_2$ mixture indicated that diverse rhodium(I) complexes are active hydroformylation catalysts under mild conditions (e.g 35° and 20 to 100 atmospheres total pressure) but that rhodium complexes with the metal in other formal oxidation states such as 0 [i e $Rh_4(CO)_{12}$] or +2 [i e. rhodium(II) acetate] are inactive catalysts under similar conditions[7] The results with $Rh_4(CO)_{12}$ were somewhat difficult to reconcile with earlier reports[9,10] that $Rh_4(CO)_{12}$ is an active hydroformylation catalyst for 1-heptene and related liquid substituted olefins. The observed inverse CO pressure dependence on the hydroformylation reaction[11] suggested that a 1 : 1 : 1 $CO/C_2H_4/H_2$ mixture might be too rich in CO for $Rh_4(CO)_{12}$ to function as an active ethylene hydroformylation catalyst Therefore the reaction of $Rh_4(CO)_{12}$ with $CO/C_2H_4/H_2$ mixtures containing variable amounts of CO were investigated in *n*-tetradecane solution at 37° and at partial pressures 12 atmospheres each of C_2H_4 and H_2 The following results were obtained relating to the production of propionaldehyde identified by its ν(CO) frequency at 1738 cm^{-1}

(1) No hydroformylation $CO/C_2H_4/H_2$ mixtures with the ratios 1 0/1 0/1 0 and 0 4/1 0 1 0 respectively

(2) Slow hydroformylation $CO/C_2H_4/H_2$ mixtures with the ratios 0 3/1 0/1 0 and 0 1 1 0 1 0

(3) Fast hydroformylation . $CO/C_2H_4/H_2$ mixtures with the ratio 0 2/1 0/1 0

Thus the maximum rate of hydroformylation was obtained under these conditions using a $CO/C_2H_4/H_2$ ratio of 0 2/1 0/1 0. Gas mixtures appreciably richer or poorer in CO led to far slower reaction rates Thus our previous failure[7] to observe ethylene hydroformylation with $Rh_4(CO)_{12}$ was a consequence of using a gas mixture far too rich in CO.

These observations suggested that the reaction of $Rh_4(CO)_{12}$ with a C_2H_4/H_2 mixture might generate catalytically active intermediates for the hydroformylation reaction In this connection the reaction of $Rh_4(CO)_{12}$ with a 1 : 1 C_2H_4/H_2 mixture in *n*-tetradecane solution at 35° and 6 atmospheres total pressure was monitored in the high pressure infrared cell (Fig 1) This reaction

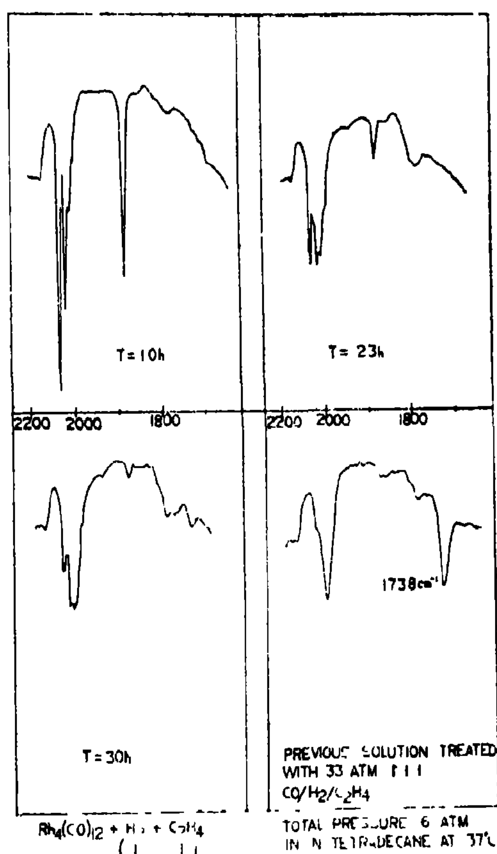
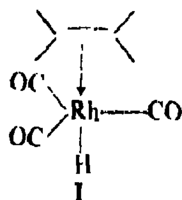


Fig. 1. Infrared specta obtained upon heating $Rh_4(CO)_{12}$ in *n* tetradecane solution under a 1 : 1 mixture of C_2H_4 and H_2 at 6 atmospheres total pressure (a) upper left after 1 hr at 37°, (b) upper right after 23 hr at 37°, (c) lower left after 30 hr at 37°; (d) lower right previous solution treated with a 1 : 1 : 1 $CO/H_2/C_2H_4$ mixture at 33 atmospheres total pressure showing the 1738 cm^{-1} band of the propionaldehyde produced by the hydroformylation reaction

gradually resulted in disappearance of the $Rh_4(CO)_{12}$ bridging ν(CO) frequency at 1883 s cm^{-1} with the production of a new species exhibiting ν(CO) frequencies at 2075 w and 2026 s cm^{-1} The pattern of these ν(CO) frequencies is consistent with that expected for a trigonal bipyramidal structure [with C_{3v} local symmetry for $HRh(CO)_3(C_2H_4)$ [Calculated from group theory[12] for ν(CO) frequencies A_1 (weak ir)+E(strong ir)] Furthermore, in some of the better resolved spectra (e g Fig 1, lower left) the 2026 cm^{-1} band assigned to the E mode is split apparently owing to some reduction of the local C_{3v} symmetry by the ethylene ligand This new species, unlike the different species formulated as $C_3H_5Rh(CO)_4$[7], persists in *n*-tetradecane solution upon release of the C_2H_4/H_2 pressure The regime of stability of the presumed $HRh(CO)_3(C_2H_4)$ is quite different than that of $HRh(CO)_4$ [reported[8] ν(CO) in dodecane . 2070 m, 2039 s, 2008 vw] which is only

stable at CO pressures around 1000 atmospheres and presumably higher. A solution of the presumed $HRh(CO)_3(C_2H_4)$ obtained by this method was shown to be an active ethylene hydroformylation catalyst using a 1 : 1 . 1 $CO/C_2H_4/H_2$ gas mixture for which $Rh_4(CO)_{12}$ is inactive as a hydroformylation catalyst.



The following additional properties of the presumed $HRh(CO)_3(C_2H_4)$ are significant :

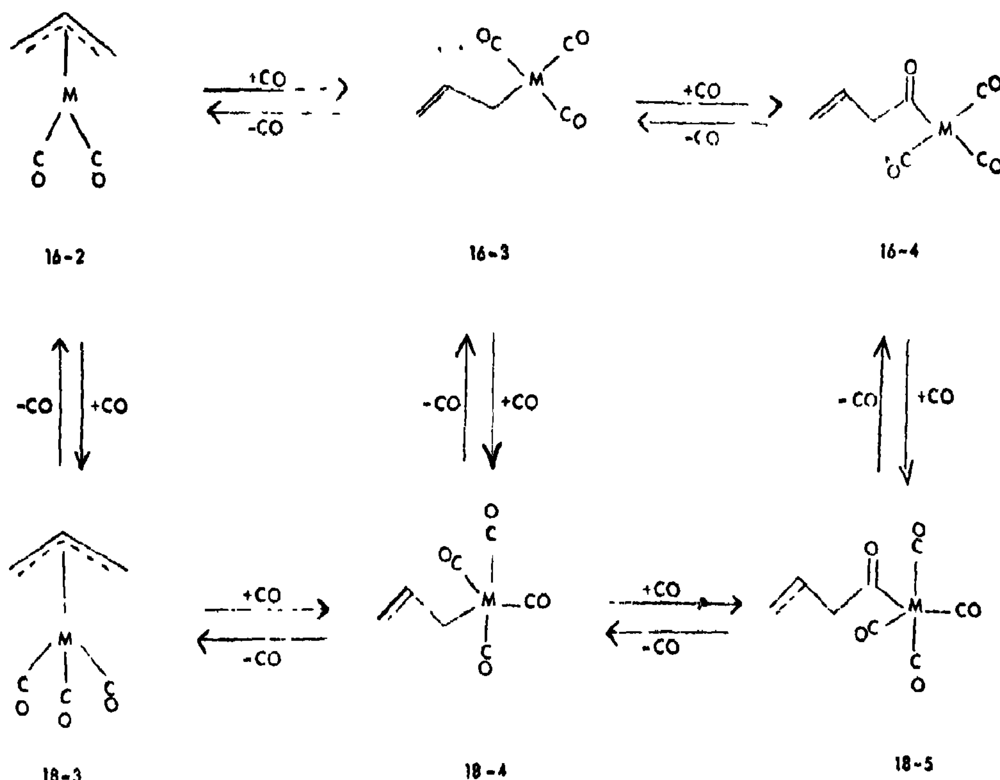
(1) It can be generated on a preparative scale by the reaction of $Rh_4(CO)_{12}$ with a 1 1 C_2H_4/H_2 mixture in an autoclave in pentane solution at room temperature and 50 atmospheres total pressure However, all attempts up to the present time to isolate $HRh(CO)_3(C_2H_4)$ from its solutions have failed since it appears to decompose upon removal of the solvent

(2) Treatment with CO alone results in the regeneration of $Rh_4(CO)_{12}$, identified by its $\nu(CO)$ frequencies A possible mechanism for this process involves ethylene displacement with CO to give $HRh(CO)_4$ which would then clusterify rapidly to $Rh_4(CO)_{12}$

Our inability to isolate the presumed $HRh(CO)_3(C_2H_4)$ combined with the lack of suitable model compounds for a more detailed interpretation of its $\nu(CO)$ frequencies than the general group theoretical arguments mentioned above has prevented us from identifying this substance by fully satisfactory and definitive methods The studies described below on the reactions of the trihaptoallyl derivatives $C_3H_5M(CO)_n$ (M=Co, n=3 ; M=Rh, n=2) were therefore initiated in an attempt to obtain information on the analogous propene complexes $HM(CO)_3(CH_2=CHCH_3)$ (M=Co and Rh)

Reactions of $C_3H_5Rh(CO)_2$ with CO and H_2

Successive stages of carbonylation of the 16-electron complex $C_3H_5Rh(CO)_2$ are possible involving both 16- and 18-electron species (Scheme 1) The reaction of $C_3H_5Rh(CO)_2$ (16-2 in Scheme 1) with CO was followed by infrared spectroscopy in the high pressure cell in order to determine which of the species listed in Scheme 1 would be most favoured Thus an *n*-tetradecane solution of $C_3H_5Rh(CO)_2$ (16-2 M=Rh) reacts with 274 atmospheres CO with disappearance of the $C_3H_5Rh(CO)_2$ to give the following species identified by their $\nu(CO)$ frequencies (Fig. 2) (1) $Rh_4(CO)_{12}$ [$\nu(CO)$ 2068 vs, 2042 s, 1883 s cm^{-1} ; triangles in Fig 2] ; (2) a ketone exhibiting a $\nu(CO)$ frequency at 1720 s cm^{-1} [$\nu(CO)$ expected[19] for diallyl ketone, $CH_2=CHCH_2C(O)CH_2CH=CH_2$ 1725-1705 cm^{-1}], (3) another rhodium carbonyl derivative exhibiting strong $\nu(CO)$ frequencies at 2022 and 2009 cm^{-1} [reported $\nu(CO)$ for $C_3H_5Rh(CO)_4$ 2115 w,



Scheme 1 Possible successive stages of carbonylation of allylmetal carbonyls of the Co/Rh/Ir triad

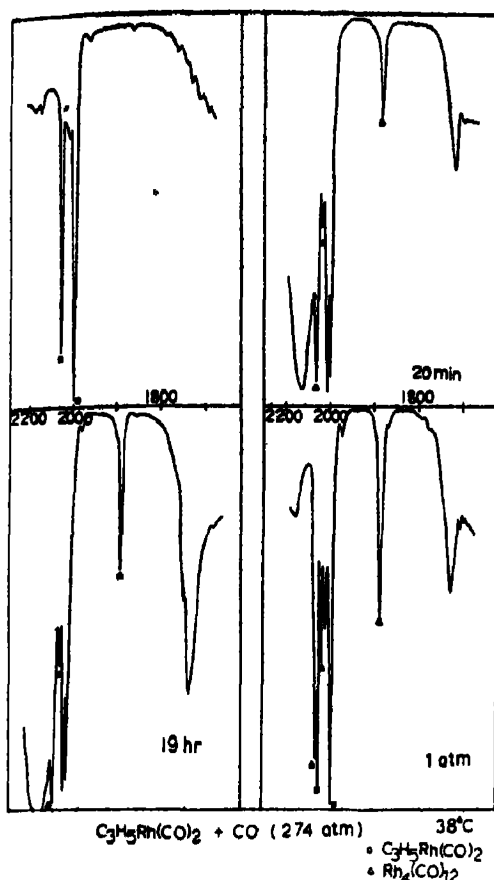
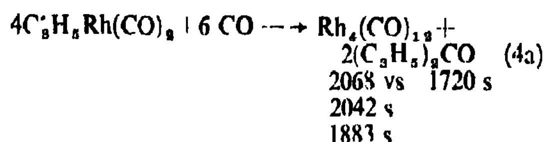


Fig 2 Infrared spectra obtained by heating $C_3H_5Rh(CO)_2$ in *n*-tetradecane solution under 274 atmospheres CO at 38°, (a) upper left . initial solution , (b) upper right , solution after 20 minutes at 38° ; (c) lower left , solution after 19 hr at 38° , (d) lower right solution obtained after releasing the CO pressure from the previous solution

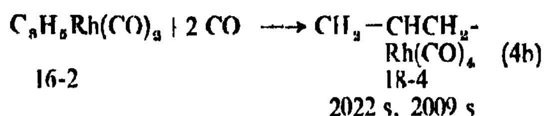
2037 s, and 2019 s cm^{-1}]. The last rhodium carbonyl derivative could be either $CH_2{=}CHCH_2$-$Rh(CO)_4$ [reported[14] ν(CO) for $CH_3Co(CO)_4$: 2105 w, 2036 m, and 2019 vs cm^{-1}] or the acyl derivative $CH_2{=}CHCH_2C(O)Rh(CO)_4$ [18-5 in Scheme 1 ; reported[14] ν(CO) for $CH_3COCo(CO)_4$: 2107 m, 2048 s, 2026 s, 2007 vs, 1719 m cm^{-1}] ; the ketone ν(CO) frequency concurrently observed at 1720 cm^{-1} blocks out the region needed to differentiate between these two alternatives. Releasing the CO pressure results in the disappearance of the 2022 and 2009 cm^{-1} ν(CO) frequencies with regeneration of the 2060 and 2000 cm^{-1} frequencies of the $C_3H_5Rh(CO)_2$ precursor This indicates quite clearly that the species responsible for the 2022 and 2009 cm^{-1} ν(CO) frequencies is one of the more highly carbonylated allylrhodium carbonyl derivatives depicted in Scheme 1 (M = Rh).

These infrared spectral data provide evidence for the following reactions upon carbonylation of $C_3H_5Rh(CO)_2$.



$$4C_3H_5Rh(CO)_2 + 6\,CO \longrightarrow Rh_4(CO)_{12} + 2(C_3H_5)_2CO \quad (4a)$$

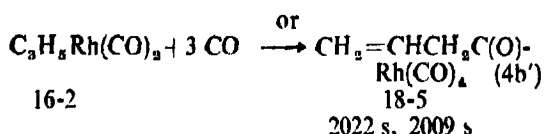
2068 vs, 2042 s, 1883 s (for $Rh_4(CO)_{12}$); 1720 s (for $(C_3H_5)_2CO$)



$$\underset{16\text{-}2}{C_3H_5Rh(CO)_2} + 2\,CO \longrightarrow \underset{18\text{-}4}{CH_2{=}CHCH_2\text{-}Rh(CO)_4} \quad (4b)$$

2022 s, 2009 s

or



$$\underset{16\text{-}2}{C_3H_5Rh(CO)_2} + 3\,CO \longrightarrow \underset{18\text{-}5}{CH_2{=}CHCH_2C(O)\text{-}Rh(CO)_4} \quad (4b')$$

2022 s, 2009 s

Reaction 4b is more plausible than reaction 4b′ since our previous work[7] showed that $C_2H_5Rh(CO)_4$ rather than $C_2H_5C(O)Rh(CO)_4$ is formed upon reactions of rhodium(I) derivatives with $CO/H_2/C_2H_4$ mixtures.

The reaction of $C_3H_5Rh(CO)_2$ (16-2 in Scheme 1) with hydrogen was also investigated Thus, treatment of a tetradecane solution of C_3H_5-$Rh(CO)_2$ with 14 atmospheres H_2 at 39° results in gradual disappearance of its ν(CO) frequencies with the appearance of a single ν(CO) frequency at 2020 cm^{-1}. The appearance of this spectrum is very similar to that obtained from the reaction of $Rh_4(CO)_{12}$ with the C_2H_4/H_2 mixture (e g. Fig. 1, lower left) suggesting its formulation as a similar type of rhodium carbonyl derivative We therefore suggest formulation of this species as $HRh(CO)_3$-$(CH_2{=}CHCH_3)$ formed according to equation 3 (M=Rh, n=2) The extra CO required for equation 3 must come from decomposition of some of the $C_3H_5Rh(CO)_2$. In this connection significant amounts of metallic rhodium were found in the infrared cell after completion of the experiment

Reactions of $C_3H_5Co(CO)_3$ with CO and H_2.

The carbonylation of the trihaptoallylcobalt derivative $C_3H_5Co(CO)_3$ (18-3 in Scheme 1, M=Co) appears to proceed in a manner analogous to that of the related rhodium derivative C_3H_5Rh-$(CO)_2$ (16-2, M=Rh in Scheme 1) Thus, heating an *n*-tetradecane solution of $C_3H_5Co(CO)_3$ [ν(CO) 2063 m and 1996 vs cm^{-1} as in Fig 3, upper left] under 173 atmospheres CO at 95° results in the gradual appearance of new bands at 2045 and 2022 cm^{-1} (Fig 3, upper right) which persist upon cooling to room temperature under pressure (Fig 3, lower left) but disappear upon decreasing the pressure to atmospheric (Fig. 3, lower right) The failure for an acyl carbonyl ν(CO) frequency around 1720 cm^{-1} to appear and disappear concurrently with the 2045 and 2022 cm^{-1} bands suggests formulation of this new species as the alkylcobalt tetracarbonyl $CH_2{=}CHCH_2Co(CO)_4$ (18-4 in Scheme 1, M=Co) rather than the acylcobalt tetracarbonyl $CH_2{=}CHCH_2C(O)Co(CO)_4$ (18-5 in Scheme 1, M=Co) The monohaptoallyl derivative

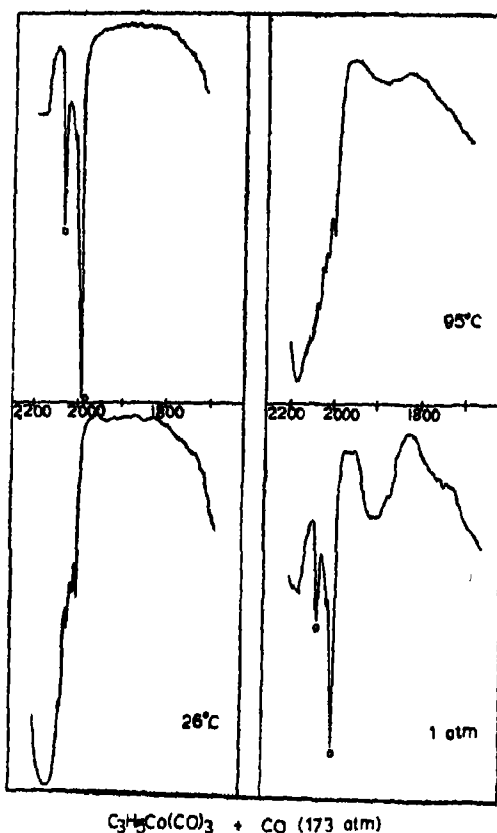


Fig 3 Infrared spectra obtained by treating $C_3H_5Co(CO)_3$ with 173 atmospheres CO : (a) upper left initial solution, (b) upper right solution obtained after heating to 95° ; (c) lower left solution obtained after cooling the previous solution to 26°, (d) lower right solution obtained by releasing the CO pressure from the previous solution

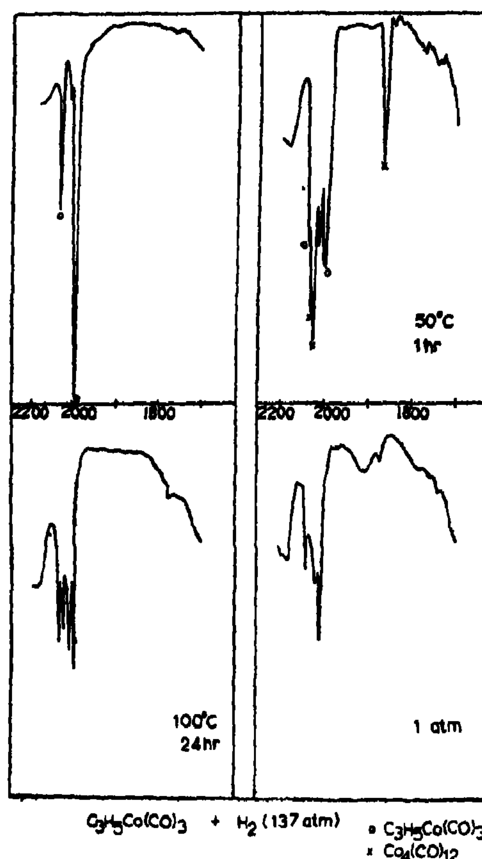


Fig 4 Infrared spectra obtained by treating $C_3H_5Co(CO)_3$ with 137 atmospheres H_2. (a) upper left · initial solution ; (b) upper right solution obtained after heating to 50° for 1 hr, (c) lower left solution obtained after heating to 100° for 24 hr, (d) lower right solution obtained by releasing the pressure from the previous solution

$CH_2=CHCH_2Co(CO)_4$ (18-4) is clearly unstable at room temperature and atmospheric pressure with respect to CO loss to give the corresponding trihaptoallyl derivative $C_3H_5Co(CO)_3$ (18-3) in contrast to the monohaptoallyl derivatives CH_2-CHCH_2-$Mn(CO)_5$[15], $CH_2=CHCH_2M(CO)_2C_5H_5$ (M = Fe[16] and Ru[17]) and $CH_2=CHCH_2M(CO)_3C_5H_5$ (M = Mo[18] and W[19]), all of which are stable at room temperature and atmospheric pressure with respect to decarbonylation to the corresponding trihaptoallyl derivatives.

The reaction of $C_3H_5Co(CO)_3$ with hydrogen was also investigated. Thus, heating an *n*-tetradecane solution of $C_3H_5Co(CO)_3$ (Fig 4, upper left) under 137 atmospheres H_2 resulted in the production of $Co_4(CO)_{12}$ [ν(CO) : 2063 vs, 2055 vs, 2038 m, 2028 m, and 1867 s cm^{-1}] at around 50° (Fig 4, upper right). Further heating to about 100° under H_2 pressure resulted in decomposition of the $Co_4(CO)_{12}$ as indicated by the disappearance of its 1867 cm^{-1} bridging ν(CO) frequency (Fig 4, lower left). Interpretation of the terminal ν(CO) region of the infrared spectrum at this point is somewhat uncertain but the ν(CO) frequencies not attributable to unchanged $C_3H_5Co(CO)_3$ could correspond those of $HCo(CO)_4$ of medium intensity or grea [reported[20] ν(CO) of $HCo(CO)_4$ 2118 vw, 2052 2029 s, and 1996 vw cm^{-1}] However, sı $HCo(CO)_4$ is not likely to be stable at 100° and CO partial pressure, formulation of this specie: $HCo(CO)_3(CH_2=CHCH_3)$ analogous to $HRh(CO$ $(CH_2=CHCH_3)$ is more probable. In any case t species appears to persist to a limited extent wl the H_2 pressure is reduced to atmospheric (Fig lower right).

The activities of the species generated fr $C_3H_5Co(CO)_3$ under various conditions for hydroformylation of ethylene have been investigat Reaction of $C_3H_5Co(CO)_3$ in *n*-tetradecane solut with a 1:1·1 mixture of $CO/C_2H_4/H_2$ at 35 atm pheres total pressure results in the formation $Co_4(CO)_{12}$ at 50° and the further conversion of t $Co_4(CO)_{12}$ to $Co_6(CO)_{16}$ above 100°. No ev d: for the production of any propionaldehyde v obtained in this system as indicated by the lack the characteristic 1738 cm^{-1} ν(CO) frequency propionaldehyde. Thus $C_3H_5Co(CO)_3$ does appear to be an active hydroformylation catalyst accord with the non-involvement of (allyl) Co(C(

species in the catalytic cycle 2a-2h (M=Co). However, the reaction of $C_3H_5Co(CO)_3$ with a 1:1 CO/H_2 mixture at 136 atmospheres total pressure results in its partial conversion at ~55° to $HCo(CO)_4$ or $HCo(CO)_3(CH_2{-}CHCH_3)$ as indicated by the formation of the 2052 m and 2029 s ν(CO) frequencies (Fig 5, upper right). This solution is an active catalyst for the hydroformylation of ethylene at 110° (Fig 5, lower left and lower right) in accord with the well-known activity of $HCo(CO)_4$ as a hydroformylation catalyst and its role in the catalytic cycle[5].

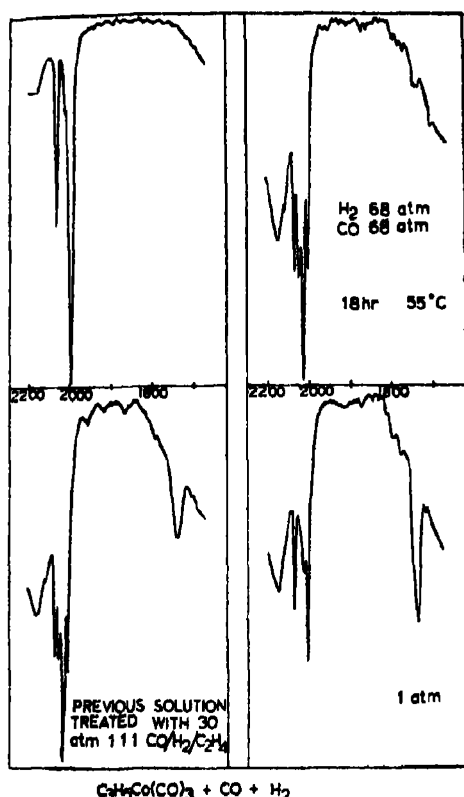


Fig 5 Infrared spectra obtained by treating $C_3H_5Co(CO)_3$ with a 1 : 1 CO,H_2 mixture (a) upper left: original solution, (b) upper right solution obtained after reaction with 136 atmospheres of a 1 1 CO/H_2 mixture at 55° for 18 hr, (c) lower left solution obtained by treatment of the previous solution with 30 atmospheres of a 1 1.1 CO/H_2/C_2H_4 mixture at 110° showing the 1738 cm^{-1} ν(CO) frequency of propionaldehyde produced in the hydroformylation reaction ; (d) lower right : solution obtained after cooling the previous solution to room temperature and releasing the gas pressure

Experimental

The infrared spectra at elevated pressures were run in the previously described[6] stainless steel high pressure infrared cell with Irtran 1 windows and recorded on a Perkin-Elmer Model 281 grating spectrometer Eastman highest purity n-tetradecane was used as the solvent for the spectra The cobalt complex $C_3H_5Co(CO)_3$ was prepared by the reaction of $NaCo(CO)_4$ with allyl iodide in tetrahydrofuran and purified by vacuum distillation The rhodium complex $C_3H_5Rh(CO)_2$[21] was prepared by reaction of $[Rh(CO)_2Cl]_2$ with $(CH_3)_3SnCH_2CH{=}CH_2$ in diethyl ether followed by washing several times with water and vacuum sublimation onto a -78° probe[22].

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The "Shaking Effect" on the Conductivities of Liquids*

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Reports on the necessity to shake the solution prior to conductivity measurements are briefy reviewed Conductivity measurements on dilute sodium chloride solutions revealed an increase in conductivity by rocking the solution prior to measurement It is proposed that part of the energy provided to the system by rocking is stored in different degrees in the various hierarchic levels of the solution It is proposed that the increased structural and energetic differentiation produced in this way is maintained dynamically and responsible for memory effects in liquids

MEMORY effects in the solid state are well-established[1,2], but their occurrence in the liquid state is hardly accepted As the high relaxation rates are further increased by increasing the energy content of a liquid phase[3], it is usually believed that random distribution is more readily "established" as the energy content of the system is increased However, random distribution is not a fact, but rather the outcome of the interpretation of statistical results According to the statistical treatment, the so-called "mean values" are attributed to the different parts of the system The consequences of this procedure lead rather to idealizations than to an understanding of the actual differentiation of matter, energy and information within the system under consideration, which appeared unaccessible so far

One of the idealizations, which appears to make it difficult to consider seriously memory effects in liquids, is that of reversibility This seems to have prevented systematic investigations on the effects of mechanical actions on various properties in the liquid state All kinetic investigations are carried out under the action of mechanical forces and the same applies to many thermodynamic measurements Shaking effects on the conductivities of solutions have been repeatedly reported, although usually just mentioned in the experimental sections.

45 years ago Hartley and Donaldson[4] mentioned an increase in conductivities of various aqueous electrolyte solutions with time, notably in very dilute solutions They obtained consistent readings after stirring the solution by completely inverting the vessel many times. Similar observations were made by Swift[5] and by Monk[6], who noticed that the resistance readings in the more dilute solutions drifted steadily They reported that these effects could be overcome by shaking the cell Such effects were also observed by James[7] The opposite effect, namely a decrease in conductivity after shaking was found for highly purified water[8]. Because shaking produced an increase in conductivity in the presence of traces of ammonia, these effects were attributed to the removal and introduction of carbon dioxide respectively Gutmann[9-13] repeatedly mentioned the necessity of prolonged shaking or stirring various non-aqueous solutions prior to resistance measurements Ames and Sears[14] also reported the increase in conductivities in more dilute solutions, even though temperature equilibrium had been established. They found the measured resistance reproducible, if the cells were manually manipulated in a manner as to change the solution between the electrodes immediately prior to measurement

Prue and Sherrington[15] found that even after thermal equilibrium had been established, the resistance of the solutions decreased slightly with time, the resistances determined immediately after rocking the cell were constant within the accuracy of the measurements and were taken as correct The so-called "shaking effect" was found more pronounced with aqueous solutions than with solutions in methanol or in dimethylformamide and much more pronounced the smaller the electrolyte concentration The changes in resistance 20 min after rocking the cell were upto 30% for the pure solvents, but hardly measurable at concentrations well above 10^{-3} *M*

More recently, similar memory effects have been reported for the electric conductivity in liquid metal alloys Miller, Paces and Komarek[16] found that the conductivities of liquid cadmium-antimony alloys containing 60 to 70% cadmium increase smoothly with increasing temperature, the liquid being mixed quite thoroughly before any readings were taken. They found the values at any given temperature different on initial heating and on subsequent cooling. After the initial heating-cooling cycle, the conductance data, on further cyclyng, reproduced the cooling curves. It may be mentioned in this connection that Scheil and Baach[17] observed that the activity of cadmium in cadmium-antimony melts is dependent on the

* Dedicated to Professor R. C. Mehrotra on the occasion of his 60th birthday.

history of the melt, and that liquids formed by melting the stable solid have a lower activity than melts which had been heated well above the liquidus temperature.

Thus, shaking and memory effects appear well-established for various electrolyte solutions as well as for metallic melts. They depend not only on the nature of the solvent and of the solute but also on the concentration of the latter It has been suggested by various authors that the shaking effect for electrolyte solutions may be due to changes in concentrations of dissolved gases but experiments under defined conditions appear not to have been made It has also been suggested that the effects may also depend on the nature of the electrode and the highly specific interaction between electrode and solution[4,7,10].

Experimental

10^{-1} *M* stock solutions of NaCl in distilled water were prepared and stepwise diluted to c 10^{-2}, 10^{-3} and 10^{-4} respectively Conductivity measurements were carried out at 22 30 ±0 03° by means of a Wayne Kerr Autobalance Universal Bridge B 642 and a thermostated cell with blank platinum electrodes (cell constant at 0 3583 cm^{-1}). The temperature in the cell was measured by a Lauda digital thermometer, which was removed from the solution as the reading was taken.

Measurements were made before and after rocking the sample by hand about 150 times in one minute By this procedure the temperature of a 100 ml sample of the solution was found to increase by about 1.8°. Specific effects between electrode and solution in the course of rocking have been excluded by carrying out the rocking in Erlenmeyer flasks prior to introduction into the conductivity vessel After full thermal equilibrium has been established, the conductivities were measured and found persistently higher after rocking the cell. For a 10^{-3} *M* solution the amount of dissolved oxygen was measured polarographically and found 2.18 10^{-3} mole O_2/litre The oxygen content was found to increase by the action of rocking to 2 33 × 10^{-3} mole O_2/litre.

TABLE 1—SPECIFIC CONDUCTIVITIES OF NaCl SOLUTIONS IN $Ohm^{-1}.cm^{-1}$.

w. obtained by dilution *without* rocking
r. *rocked*

$10^{-1}M$		$10^{-2}M$		$10^{-3}M$
3.12×10^{-3}	$\xrightarrow{w}$	8.40×10^{-4}	$\xrightarrow{w}$	1.142×10^{-4}
↓ *r*		↓		↓ *r*
				1.555×10^{-4}
		8.70×10^{-4}	$\xrightarrow{w}$	1.161×10^{-4}
				↓ *r*
				1.165×10^{-4}
3.38×10^{-3}	$\xrightarrow{w}$	8.60×10^{-4}	$\xrightarrow{w}$	1.165×10^{-4}
		↓ *r*		↓ *r*
				1.180×10^{-4}
		8.70×10^{-4}	$\xrightarrow{w}$	1.174×10^{-4}
				↓ *r*
				1.171×10^{-4}

The results show that at different NaCl concentrations the solutions had higher conductivities after rocking Such rocking effects were partly preserved even through the dilution steps No decrease was observed on standing for 2 weeks

Discussion

The results cannot be interpreted on ground of the current views Structural, thermodynamic and kinetic data do not provide access to the differentiations within a given system According to a non-statistical approach proposed recently[18-25] the structural differentiation which is disguised in the statistical data[26], has been illustrated by the application of the so-called bond length variation rules of the extended donor-acceptor approach[26,27] It has been shown that such differentiations must be dynamically maintained and highly influenced by the actual environmental conditions[18,19,28] The strictly determined individual motions require the existence of relations between stronger and weaker, outside and inside, before and after.

The properties of the parts constituting the phase under consideration are different with regard to their *energy content per part*, their adaptability towards changes, their influence on the environment and their capability to accept and to store energy and information[28]. The ordering with regard to their individual significance within the whole phase and for the whole phase has lead to distinguish different groups of particles The continuous interrelationships between them are characteristic for a so-called "hierarchic order" as reflected in the "hierarchic organization" of the parts within the system[18-28] In each of the different groups the parts are found to serve the system in different ways, i e, on different hierarchic levels. A level is hierarchically higher the greater its significance for the whole system, the greater its range of influence, its adaptability towards changes, the energy content and the energy storage capability per part[19].

The highest observable hierarchic level within a condensed phase is that of the phase boundary, which is continuously changing according to its dynamic interactions with the environment and with the other parts of its phase[18,20] The parts serving this level are not in thermal equilibrium and hence they may contain information about the history of the system. The historical information is not completely lost, although the parts are continuously exchanged between the levels. This is because information is not stored within the single parts of the system themselves, but maintained by the ordered dynamics within the collective[28].

The dissolved particles as well as the so-called "voids" influence each other "through" the "solution-structure" and they are under the decisive influence of the forces acting on the surface level They have been referred to as "structure modifying and modified centres" ("SMM-centres"). They exert a decisive influence on the system properties Solute particles, such as ions serve on a level which is hierarchically superior to that of the so-called "uncoordinated" solvent molecules, which may be referred to as "normal solvent molecules".

By the application of mechanical forces to a solid material, such as grinding or the action of cold-work, part of the energy applied remains in the system, where it is distributed over the various hierarchic levels according to their different adaptabilities[29]. Thus, the system is increased in structural and in energetic differentiation in that it mobilizes its own dynamic order to maintain its "individuality"[9]

Likewise, shaking or stirring a solution leads to a limited energy increase of the system The total gain in energy may be statistically insignificant and too small to be measurable, and yet it may result in a more or less pronounced increase in structural and energetic differentiation within the liquid system The parts in higher levels gain energy, whereas the parts in the lowest level may even be lowered in energy The number and stabilities of voids appear to be increased. This is in agreement with the increase in oxygen content found after rocking, although it cannot be said in what way the dissolved oxygen contributes to the system stabilization

The slightly exothermic dissolution process of sodium chloride in water leads to a lowering of the total energy content of the system The dissolved ions gain energy and become more strongly hydrated. Thus, energy must be provided from the vast amount of the so-called "normal" solvent molecules Due to their large number, the energy loss per solvent molecule is unmeasurably small but the gain in energy per ion is more significant[29] The differentiation of the energy pattern is further increased by rocking the solution Most of the extra energy is taken up by the ions. Each of them is stabilized by stronger hydration and also made more mobile; *the conductivity of the solution is increased.

The remarkable memory effect to the rocking treatment seems to be due to the gain in stabilities of the hydration structures, which are preserved dynamically in their leading role for the system properties. We have observed analogous memory effects after heating the sodium chloride solutions; their conductivities at room temperature are found higher than those of the solutions which had not been heated.

Likewise, the observations on the conductivities of cadmium-antimony alloys[16] may be reinterpreted. As the system is heated, it becomes energetically more differentiated In a metallic conductor the conductivity is decreased accordingly. The greater differentiation is not completely lost by lowering the temperature: after heating, the conductivity is somewhat lower and the ductility greater.

Vigorous stirring of a metal melt near its melting point leads to unexpected properties which are the basis of a new casting process, the so-called "rheo-casting"[30] It will be shown in a forthcoming paper that such features are also explainable in terms of the concept of the hierarchic organization of matter.

Concluding Remarks

The unusual interpretation of the hardly appreciated "shaking effect" leads to a number of questions which may lead to appropriate experiments. It would be expected, for example, that by vigorous shaking of a highly diluted aqueous solution, its surface tension, its vapour pressure and its rate of solvolysis should change. It may further be expected that many other effects, which have been neglected so far, may find their place within the framework of the concept of the hierarchic organization of matter In particular the question of interactions occurring at phase boundaries appears in a new light, as the hierarchically highest levels of both of the contacting phases are involved.

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Redistribution Reactions Involving Lithium Aluminium Hydride and Lithium Tetraphenylaluminate

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Redistribution reactions involving $LiAlH_4$ and $LiAlPh_4$ were performed by mixing the reagents in appropriate ratios. The products: $LiAlH_3Ph$, $LiAlH_2Ph_2$ and $LiAlHPh_3$ were isolated and characterised by elemental analysis, infrared and nmr spectroscopy and DTA-TGA analysis. These products were also prepared by the reaction of PhLi with AlH_nPh_{3-n} (where n = 1-3) in diethylether. Also $PhAlH_2$ and Ph_2AlH were prepared by the reaction of Ph_3Al and AlH_3 in both diethyl ether and THF in the appropriate stoichiometric ratios.

We have been engaged in reactions of lithium aluminium hydride with various main group metal organic compounds, e.g., phenyllithium[1], diphenyl magnesium[2] and lithium triphenylmagnesiate[3]. In order to help characterize the products of the above reactions, it was deemed necessary to prepare the expected by-products of these reactions i.e., $LiAlH_nR_{3-n}$ (where n=1-3) by an independent method. For this reason, we studied the reaction of $LiAlPh_4$ and $LiAlH_4$ in diethylether by following the progress of the reaction by ir and nmr spectroscopy and isolating the intermediate products. Zakharkin and Ivanov[4] in 1964 reported the reaction of alkali metals and their hydrides with triphenylaluminium and reported the preparation of lithium triphenylaluminium hydride. However, the product was not well characterized.

Experimental

Apparatus: Reactions were performed under dry nitrogen at the bench or in a glove box equipped with a recirculating system using manganese oxide to remove oxygen. Infrared spectra were obtained on a Perkin-Elmer 620 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded on a Varian A-60 in ether solvent. The X-ray powder diffraction pattern of $LiAlPh_4$ was obtained on a Philips-Norelco X-ray unit using a 114.6 mm camera with nickel filtered Cu-K_α radiation. The sample was sealed in 0.5 mm capillary and exposed to X-rays for 6 hr. The 'd' spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Analyses: Gas analyses were accomplished by hydrolysis of samples with HCl on a standard vacuum line equipped with a Toepler pump. Aluminium was determined by adding excess EDTA and back-titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. Lithium was determined by flame photometry. Phenyl groups present in the complexes were determined by hydrolyzing the samples with water and analyzing the filtrate for benzene by glc using an SE 30 column at 70°. Mesitylene was used as the solvent and hexanol was used as the internal standard.

Materials: Solvents were distilled immediately prior to use over $LiAlH_4$ (ether) or $NaAlH_4$ (THF, benzene and mesitylene). Phenyl lithium was prepared in benzene diluent by the reaction of iodobenzene with *n*-butyllithium dissolved in hexane. The solid product was dissolved in ether, recrystallized at −78°, redissolved in freshly distilled ether and standardized by Watson and Eastham analysis[5].

It was observed that phenyllithium cleaves diethyl ether at room temperature to give the product Li_2(OEt)Ph. Ether cleavage could be slowed down by keeping the solution at 15°.

Triphenylaluminium[6] was prepared by refluxing a mixture of diphenylmercury and aluminium chips in toluene for 40 hr and filtering the resulting mixture hot through glass wool under nitrogen pressure. The product was recrystallized in hot toluene and dried under reduced pressure (0.05 mm) for 1 hr at 60°.

Lithium aluminium hydride ($LiAlH_4$) was obtained from Ventron, Metal Hydrides Division. A solution was prepared by refluxing $LiAlH_4$ in ether overnight followed by filtration through a glass-fritted funnel using dried Celite Analytical

Filter-Aid (Johns-Mansville). The clear solution was standardized by aluminium analysis.

Lithium tetraphenylaluminate ($LiAlPh_4$) was prepared by the addition of phenyllithium in ether to triphenylaluminium in ether with continuous stirring at 0° over a period of several hr. A viscous insoluble layer separated from the ether which crystallized from solution overnight. The white solid was soluble in tetrahydrofuran, but insoluble in diethyl ether. Analysis of the white solid gave the following results: Calcd. for $LiAl(C_6H_5)_4$; Li.Al Ph=1.0:1.0·4 0. Found; 1.00:1.06:4.10.

X-ray powder diffraction data for $LiAlPh_4$ showed the following lines: 8.5 s, 6.8 w, 6 0 w-m, 5 4 vw, 4.8 vw, 4.4 vs, 4.15 s, 3 8 w, 3 25 m-s, 2 95 m, 2 82 w, 2.76 w, 2 63 w, 2.55 w, 2 43 w, 2 3 vc, 2 25 vw, 2 13 vw, 2 05 vw, 2 00 vw, 1 90 w, 1 78 w, 1 58 w.

Redistribution of $LiAlH_4$ and $LiAlPh_4$ as determined by infrared analysis: A 0 615 *M* solution of $LiAlH_4$ in ether was added in increments to a magnetically stirred slurry of $LiAlPh_4$ in ether at room tempe ature. When the ratio of $LiAlH_4$ to $LiAlPh_4$ was 1.3 a clear solution resulted. After each addition the solution was stirred for 1 hr at room temperature. Infrared spectra were obtained by withdrawing samples of the solutions under nitrogen via syringe The additions were continued until $LiAlH_4$ was in excess Fig 1 shows the infrared spectra obtained in this study.

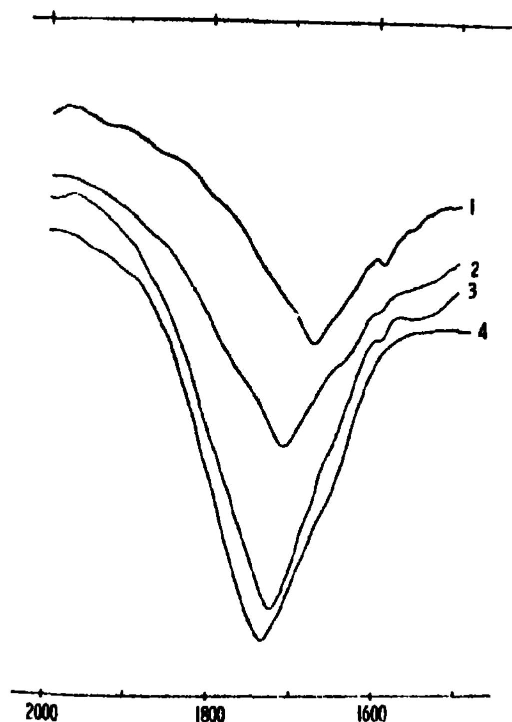


Fig 1 Infrared spectra of solutions obtained by adding $LiAlH_4$ to $LiAlPh_4$ in diethyl ether in ratios (1) 1 : 3, (2) 1 : 1, (3) 3 . 1, (4) pure $LiAlH_4$.

Preparation of $LiAlH_3Ph$· To a slurry of $LiAlPh_4$ (1.78 g; 5 2 mmoles) in ether was added 37 6 ml of 0 615 *M* solution of $LiAlH_4$ in ether (15 6 mmoles) at room temperature with continuous stirring. A clear solution resulted and the reaction mixture was stirred for an additional hr. The excess ether was removed under reduced pressure to give a viscous product which on standing at room temperature for 5 days produced crystals Elemental analysis of the crystals gave the following ratios Li.Al.H Ph.ether = 1 02 1 00·3 03 0 97 2 10 Calcd for $LiAlH_3Ph.2Et_2O$=1 00 1 00:3 00.1.00.2 00 The infrared spectrum in ether was similar to the spectrum shown in Fig. 1

Preparation of $LiAlH_2Ph_2$· To a slurry of $LiAlPh_4$ (2 839 g, 8.30 mmoles) in ether was added dropwise 20 ml of 0 615 *M* solution of $LiAlH_4$ in ether (8.30 mmoles) with constant stirring. This reaction mixture was stirred for 1 hr after a clear solution was obtained The ether was removed under vacuum producing a pasty mass which crystallized after keeping for 3 days at room temperature Elemental analysis gave the following ratios. Li.Al:H.Ph Et_2O = 1 02 1 00 2 06 1 98 1 94 Calcd. for $LiAlH_2Ph_2$ $2Et_2O$–1 00 1 00 2 00 2 00 2.00.

Preparation of $LiAlHPh_3$· To a slurry of $LiAlPh_4$ (6 26 g; 12 45 mmoles) in ether was added dropwise 10 0 ml of 0 615 *M* solution (4 15 mmoles) of $LiAlH_4$ in ether. The resulting solution was stirred for 1 hr followed by removal of excess solvent under vacuum When about 10 ml of ether remained, a white crystalline solid appeared which was separated by decantation, washed with ether and dried at room temperature under reduced pressure (0 05 mm) for 15 min The crystalline product then changed to a viscous product When freshly distilled ether was added to this viscous product, it again changed to a crystalline solid The solid was separated and dried at 0° for 1 hr under vacuum (0 05 mm) and then analyzed Elemental analysis gave the following ratio: Li 1 H Ph ether=1 05 1 00 0 97 3 03: 4 04 Calcd. for $LiAlHPh_3$ $4Et_2O$–1 00.1 00 1 00: 3 00 4.00.

Redistribution reaction of AlH_3 with $AlPh_3$ in ratios (i) 1 2, (ii) 2 1 in THF and diethyl ether

(i) Reaction of AlH_3 with $AlPh_3$ in 1 2 ratio

(a) *In THF* To a well-stirred solution of Ph_3Al (10 0 mmoles) in THF (30 ml) was added dropwise 5 0 mmoles of AlH_3 solution in 15 ml of THF The reaction mixture was stirred for 15 hr at room temperature and the solution analyzed Anal: Calcd for $AlHPh_2$ Al:H Ph = 1 00:1 00:2 00. Found. 1 00 0 94 2 03 IR showed a strong band at 1782 cm^{-1} due to νAl-H stretching. NMR analysis of the solution showed two multiplets due to the *ortho* (δ 7.7 ppm) and *meta-para* (δ 7.19 ppm) protons of the phenyl groups downfield to the THF signals, in the ratio of 2 3

(b) *In diethyl ether*: When 7.0 mmoles of AlH_3 solution in diethyl ether (20 ml) was added to a well-stirred slurry of Ph_3Al (14.0 mmoles) in 30 ml of diethyl ether, a clear solution resulted in 15 min of stirring. The reaction mixture was stirred for approximately 10 hr and analyzed. Anal: Calcd. for $AlHPh_2$ Al:H.Ph = 1.00.1.00.2.00. Found · 1.00:0.97:2.02. The infrared spectrum of the solution showed the presence of νAl-H stretching at 1865 cm^{-1}.

(ii) Reaction of AlH_3 with Ph_3Al in 2.1 ratio.

(a) *In THF:* 9.4 mmoles of AlH_3 solution in THF (25 ml) was added to a well-stirred solution of Ph_3Al (4 7 mmoles) in THF (20 ml) at room temperature and the reaction mixture stirred The completion of the reaction was monitored by the complete disappearance of νAl-H at 1760 cm^{-1} (due to AlH_3) and its appearance at 1770 cm^{-1} (due to $PhAlH_2$) The solution was analyzed Anal . Calcd for AlH_2Ph Al.H:Ph = 1 00 2 00:1 00 Found : 1 00 1 90.1 03 ; An nmr spectrum of the product in THF showed two sets of multiplets centered at δ 7.73 ppm (due to *ortho* protons of the phenyl groups) and 7 23 ppm (due to *meta-para* protons of the phenyl groups) in the ratio 2·3

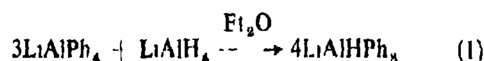
(b) *In diethyl ether* When the above reaction was carried out in diethyl ether solution, a clear solution resulted Analysis of this solution showed that it contained Al, H, and Ph in ratios 1 00. 1 93 1 01. An infrared spectrum of the reaction solution showed the presence of νAl-H at 1845 cm^{-1}.

Reaction of PhLi with $AlH_nPh_{(3-n)}$ in diethyl ether

A diethyl ether solution of freshly prepared phenyllithium was added to a well-stirred solution of phenylaluminium hydride, $AlH_nPh_{(3-n)}$ in equimolar proportions and the reaction mixture stirred at room temperature for approximately 1 hr The resulting solution was analyzed and infrared spectrum recorded Results are given in Table I

spectrum of $LiAlPh_4$ in THF showed the presen of two multiplets downfield to the THF multipl due to *ortho* and *meta-para* protons of the phen groups. The internal chemical shifts, δ int between the *ortho* (lower multiplets) and *meta-pa* (upper multiplet) protons of the phenyl groups wer observed to be 0.60 ppm. In the case of phenyl lithium, the internal chemical shifts, between th *ortho* and *meta-para* proton multiplets were foun to be 0 99 ppm at room temperature while in th case of triphenylaluminium, it was found to be 0 51 ppm. Ladd[7] has shown that protons *ortho* to the metal-carbon bond in phenylmetallic compounds experience a large deshielding effect He has further shown that metals of lower electronegativity produce greater deshielding of the *ortho* protons and increased δ int. We have also noticed the same effect in the case of phenyllithium and triphenylaluminium, the former being more electropositive, gave a larger δ int compared to the more electronegative aluminium

The redistribution of $LiAlH_4$ and $LiAlPh_4$ was studied by adding an ether solution of $LiAlH_4$ to an ether slurry of $LiAlPh_4$ in 1:1, 1 3 and 3·1 ratios followed by infrared analysis of the resulting solutions (Fig. 1). When an ether solution of $LiAlH_4$ was added dropwise to a well stirred slurry of $LiAlPh_4$ in 1.3 ratio in diethyl ether at room temperature, a clear solution was obtained.



$$3LiAlPh_4 + LiAlH_4 \xrightarrow{Et_2O} 4LiAlHPh_3 \quad (1)$$

An infrared spectrum of the resulting solution showed the presence of a strong band at 1730 cm^{-1} due to Al-H stretching ($LiAlH_4$ shows Al-H stretching at 1740 cm^{-1} in diethyl ether) However, when the excess of solvent was removed under reduced pressure, a viscous colorless liquid resulted which on standing at room temperature for 5 days gave crystals that analyzed for $LiAlHPh_3 \cdot 2Et_2O$ The infrared spectrum of these crystals dissolved in diethyl ether showed the presence of Al-H stretching

TABLE I—REACTIONS OF PhLi WITH $AlH_nPh_{(3-n)}$

Exp. No	Reactants (mmoles) PhLi	$AlH_nPh_{(3-n)}$	Solvent (ml)	Analysis (Ratio) Li	Al	H	Ph	Product	IR νAl-H (cm^{-1})
1.	5 5	AlH_3 (5 5)	45	1.03	1.00	2.92	1 05	$LiAlH_3Ph$	1730
2.	4 5	AlH_2Ph (4 5)	50	1.02	1.00	1.93	2.04	$LiAlH_2Ph_2$	1710
3.	5 5	$AlHPh_2$ (5 5)	55	1 04	1.00	0 95	3 07	$LiAlHPh_3$	1680

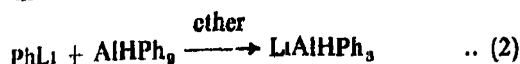
Results and Discussion

In order to study the redistribution of $LiAlPh_4$ and $LiAlH_4$, it was necessary to prepare $LiAlPh_4$ in the pure state. For this study, $LiAlPh_4$ was synthesized by the reaction of PhLi with Ph_3Al in diethyl ether and characterized by elemental analysis and X-ray powder diffraction studies. The nmr

at 1730 cm^{-1} The nmr spectrum of the ether solution showed two multiplets due to *ortho* and *meta-para* protons of the phenyl groups The internal chemical shift, δ int., was found to be 0 60 ppm.

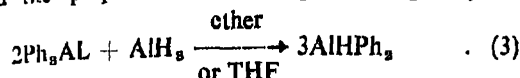
The product, $LiAlHPh_3$, was also prepared by the reaction of PhLi with $AlHPh_2$ in diethyl ether (Eq. 2). Diphenylaluminium hydride was prepared

y the redistribution reaction of aluminium hydride



$$PhLi + AlHPh_2 \xrightarrow{\text{ether}} LiAlHPh_3 \quad .. (2)$$

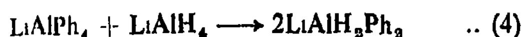
with triphenylaluminium in 1:2 ratio in THF as well as in diethyl ether (Eq. 3). In 1964, Surtees[8] reported the preparation of $AlHPh_2$ and AlH_2Ph by the



$$2Ph_3AL + AlH_3 \xrightarrow[\text{or THF}]{\text{ether}} 3AlHPh_2 \quad . (3)$$

redistribution reaction of AlH_3 and Ph_3Al in the appropriate ratio in refluxing benzene. He reported the nmr spectra of the products in dichloromethane to contain only one set of multiplets due to phenyl protons However, during our studies in THF solvent, we obtained two sets of multiplets explainable due to the *ortho* and *meta-para* protons of the phenyl groups.

When $LiAlH_4$ was added to $LiAlPh_4$ in 1.1 molar ratio, the band due to Al-H stretching shifted to 1710 cm^{-1} A highly viscous liquid resulted when an excess of solvent was removed under vacuum. However, the viscous liquid produced crystals on standing for 3 days at room temperature Elemental analysis showed the product to be $LiAlH_2Ph_2$ The nmr spectrum of an ether solution of $LiAlH_2Ph_2$ showed two multiplets due to *ortho*

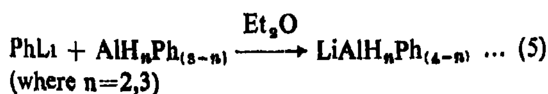


$$LiAlPh_4 + LiAlH_4 \longrightarrow 2LiAlH_2Ph_2 \quad .. (4)$$

and *meta-para* protons of the phenyl ring; the internal chemical shift was 0.61 ppm.

When the ratio of reacting solutions of $LiAlPh_4$ to $LiAlH_4$ was 3:1 in diethyl ether, a broad band centered at 1680 cm^{-1} was observed in the infrared spectrum due to Al-H stretching. When an excess of solvent was removed under reduced pressure, a crystalline solid appeared. These crystals were analyzed and were consistent with the compound $LiAlHPh_3$ $4Et_2O$. When these crystals were dried under vacuum at 25°/0 05 mm for 1/2 hr, a viscous liquid resulted which corresponded, by analysis, to $LiAlHPh_3$ $2Et_2O$ When a small amount of ether was added to this viscous liquid, it became crystalline immediately The infrared spectrum of these crystals in ether showed an Al-H stretching band at 1680 cm^{-1} and the internal chemical shift in the nmr spectrum due to the phenyl ring was found to be 0 62 ppm

The products $LiAlH_2Ph_2$ and $LiAlHPh_3$ were also prepared by the reactions of phenyllithium with phenylaluminium hydride ($PhAlH_2$) and AlH_3 respectively (Eq. 5). The resulting products exhibited Al-H stretching bands similar to those reported above for the same products prepared by the redistribution of $LiAlH_4$ and $LiAlPh_4$.



$$PhLi + AlH_nPh_{(3-n)} \xrightarrow{Et_2O} LiAlH_nPh_{(4-n)} \quad ... (5)$$

(where n=2,3)

All of the $LiAlH_nPh_{4-n}$ compounds were soluble in diethyl ether and THF and the solubility in diethyl ether increased with the number of hydride groups.

The vacuum DTA-TGA data for the $LiAlH_n$-Ph_{4-n} compounds are given in Table 2 It seems that these products first disproportionate to give $LiAlH_4$ and $LiAlPh_4$ and then the $LiAlH_4$ further decomposes to give Li_3AlH_6. The detailed decomposition scheme for $LiAlH_2Ph_2.Et_2O$ is given below (See also Fig. 2)

TABLE 2—THERMAL DECOMPOSITION OF LITHIUM HYDRIDO-PHENYLALUMINATES.

Compound	Thermicity	Range of transition (peak max), °C	% wt. loss
$LiAlH_2Ph_2$ $2Et_2O$	Endo	55-90 (70)	24.2
	Endo	90-120 (98)	20.1
	Exo	170-200 (190)	0.55
	Endo	200-225 (210)	0.55
	Endo	280-350 (320)	40 2
$LiAlH_3Ph.2Et_2O$	Endo	60-125 (90)	56.2
	Exo	165-190 (180)	0.58
	Endo	190-215 (197)	0.28
	Endo	270-350 (315)	28.3
$LiAlHPh_3$ $4Et_2O$	Endo	50-150 (110)	52.1
	Exo	165-195 (185)	0.11
	Endo	195-220 (200)	0.06
	Endo	295-348 (318)	32 3

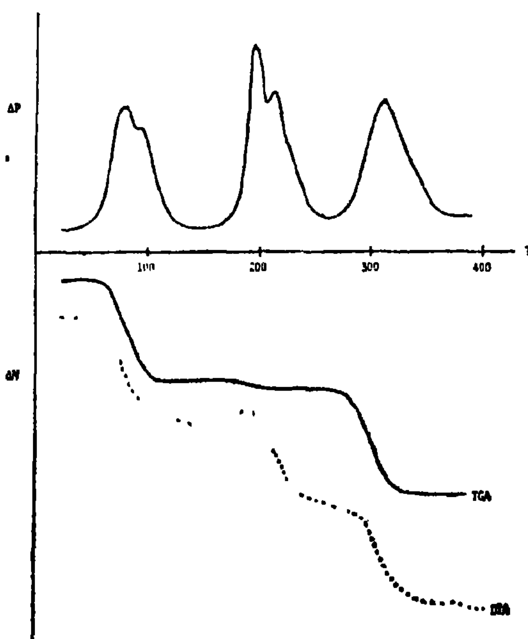
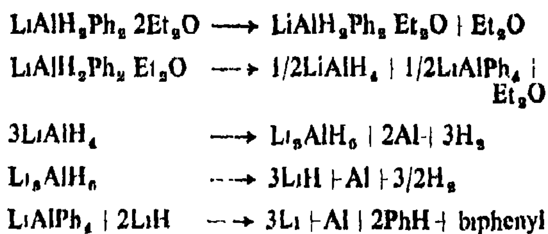


Fig. 2. Vacuum DTA-TGA of $LiAlH_2Ph_2$ Et_2O



$$LiAlH_2Ph_2 \cdot 2Et_2O \longrightarrow LiAlH_2Ph_2 \cdot Et_2O + Et_2O$$

$$LiAlH_2Ph_2 \cdot Et_2O \longrightarrow 1/2LiAlH_4 + 1/2LiAlPh_4 + Et_2O$$

$$3LiAlH_4 \longrightarrow Li_3AlH_6 + 2Al + 3H_2$$

$$Li_3AlH_6 \longrightarrow 3LiH + Al + 3/2H_2$$

$$LiAlPh_4 + 2LiH \longrightarrow 3Li + Al + 2PhH + \text{biphenyl}$$

The trappable gases were identified to be diethyl ether and benzene. It was also determined that when $LiAlPh_4$ is thermally decomposed under vacuum, it produces biphenyl.

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Substitution of η_5-Cyclopentadienyl Iron Carbonyl Halides by Diphenylcyclopropenone

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Substitution of the η_5-cyclopentadienyl iron carbonyl halides $C_5H_5Fe(CO)_2X$ by diphenylcyclopropenone (DPCP) yields the complexes $[(DPCP)_3FeX][FeX_4]$, X=Cl, Br, I in addition to ferrocene and $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ as byproducts. The reaction mechanism is discussed in terms of normal nucleophilic substitution and a possible radical process.

As an extension of our previous studies[1] of the substitution reactions of η-cyclopentadienyl iron carbonyl halides $\eta\text{-}C_5H_5Fe(CO)_2X$ (X=Cl, Br, I), the reactions of these compounds with the cyclic ketone diphenylcyclopropenone, Ph_2C_3CO, are reported below. Relatively few studies of the reactions of this nucleophile with metal carbonyl complexes have been reported although cyclopropenone metal complexes have been suggested as intermediates in carbonylation reactions of acetylenes[2]. Complexation of the ligand in a η_1 mode was previously suggested by one of us in complexes of the type $C_3H_2COFe(CO)_3$[3]. However, such complexes have not been isolated although coordination via the double bond does occur in $(PPh_3)_2$-Pt(methylcyclopropenone)[4]. In general, however it appears that DPCP which is highly polarized with a dipole moment of 5.14D[5], most frequently complexes by coordination of the oxygen lone pair to form stable metal-oxygen σ-bonds. For example, Bird and Briggs[6] isolated a series of complexes $(DPCP)_2MX_2$(M=Zn, X=Cl, Br, I, M=Co, X=Cl, Br, ClO_4, M=Ni, X=Br, ClO_4; M=Ru, X=Cl). In all of these compounds, shifts of the infrared bands in the 2000-1500 cm^{-1} region are consistent with bonding of the DPCP ligand via the oxygen atom. In the complexes $\eta\text{-}C_5H_5Fe(CO)_2L$ (L=cyclohexenone and 3-methylcyclohexenone), nmr and X-ray studies confirm the presence of an iron-oxygen σ-bond in the bonding of the ketone to the iron atom[7].

Experimental.

All solvents were refluxed over the appropriate drying agents, distilled and degassed before use. Reactions and work-up were carried out under oxygen-free nitrogen. Infrared spectra were recorded on Perkin Elmer 457 and 283 spectrometers, uv/visible spectra on a Perkin Elmer 402 spectrometer, ^1H nmr spectra on Perkin Elmer R12B and Jeol PS100 spectrometers. Microanalyses were carried out in the microanalytical laboratories of this department. Conductivity measurements were made using a Radiometer instrument (Copenhagen type CDC 304). Linear plots of molar conductances versus (concentration)$^{\frac{1}{2}}$ were extrapolated to infinite dilution.

$C_5H_5Fe(CO)_2X$ were prepared by literature methods X=Cl[8], X=Br, I[9]. DPCP was prepared from dibenzylketone[10].

Reaction of $\eta\text{-}C_5H_5Fe(CO)_2X$ and DPCP. A typical reaction is as follows. DPCP (8 mmoles) in 50 ml benzene was added to $\eta\text{-}C_5H_5Fe(CO)_2X$ (4 mmoles) in 50 ml benzene and refluxed for about 10 hr. Filtration of the hot solution, washing of the solid product twice with 5 ml cold benzene followed by n-hexane and recrystallization from CH_2Cl_2-petroleum ether (40-60°) gave tiny crystals. The filtrate was reduced in volume to about 10 ml and chromatographed on a silica gel column and eluted with benzene. The first band (yellow) eluted was identified as ferrocene and the second band (red) as unreacted $\eta\text{-}C_5H_5Fe(CO)_2X$. If the reaction was carried out at about 60°, additional bands due to $(\eta\text{-}C_5H_5)_2Fe(CO)_2$ and $[\eta\text{-}C_5H_5Fe(CO)_2]_2$ were also obtained on chromatography.

Results and Discussion

When DPCP and $\eta\text{-}C_5H_5Fe(CO)_2X$ (X = Cl, Br and I) were heated together in benzene under nitrogen, a microcrystalline precipitate formed

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within 30 min and on monitoring the reaction by infrared spectroscopy in the metal carbonyl region it was found from the decrease in intensity of the initial peaks [ν(CO) 2057, 3013 cm^{-1}, 2054, 2008 cm^{-1} and 2044, 2000 cm^{-1} for X = Cl, Br, I respectively] that the reaction rate followed the sequence Cl > Br > I. In the case of both chloride and bromide, a band at 1969 cm^{-1} developed during the reaction indicating an intermediate since the final products contain no metal-carbonyl groups (nujol mull) identical with those reported previously[12]. This compound decomposes to give (a) ferrocene and (c) the third compound isolated from the column [(η-C_5H_5)Fe(CO)$_2$]$_2$ the identity of which was proven by infrared spectroscopy. The formation of the above complexes by nucleophilic attack by DPCP on η-C_5H_5Fe(CO)$_2$X with complete displacement of both carbonyl and cyclopentadienyl ligands under relatively mild reaction conditions is surprising, especially in view of the much slower

TABLE I—PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR [(DPCP)$_2$ FeX] [FeX$_4$]

X	Decomp. Pt °C	Colour	Analysis Found (Calcd.) C	H	X	Fe	Infrared spectra (cm^{-1}) 2000-1500 region (a)	M-X region (b)	Conductivity Λ_M ohm^{-1} cm^{2}mol^{-1}
Cl	188	Lime-yellow	59.16(59.50)	3.73(3.97)	19.92(19.56)	11.81(12.34)	1859(s) 1598(s) 1579(m) 1538(s)	383	122[c]
Br	194	Dark orange	47.45(47.79)	2.44(2.65)	35.53(35.40)	10.00(9.9)	1857(s) 1597(s) 1577(m) 1537(s)	295	112[c] 145[d]

a Measured in KBr discs
b Measured in Nujol mulls
c Measured in Nitromethane
d Measured in Acetone

In general, reactant molar ratios of 1:2 (complex: ligand) were used and larger ratios simply increased the rate of reaction. The physical properties and analytical data of the complexes formed in this reaction (Table I) are consistent with their formulation as [Fe(DPCP)$_2$X][FeX$_4$] (X = Cl, Br, I) although in the case X = I the solid product was not sufficiently stable to give good analytical figures. The infrared data showed clearly the absence of any metal-carbonyl group, the shift of the higher frequency band in free DPCP from 1845 cm^{-1} to 1857-1859 cm^{-1} in the complexes and of the lower band 1618 cm^{-1} to 1598 cm^{-1} is typical of complexation of DPCP via the oxygen lone pair[9]. The far infrared region exhibited bands at 383 cm^{-1} and 295 cm^{-1} for the chloride and bromide respectively which lie very close to those reported for [NEt$_4$][FeX$_4$], X = Cl, Br[11]. The presence of the FeX$_4^-$ anion was further confirmed from the uv/visible spectra of the complexes measured in acetonitrile, for example, the chloride complex shows a band at λ_{max} 358 nm compared with λ_{max} ~360 nm for [FeCl$_4$]$^-$[11]. The ^{1}H nmr spectra measured in deuterated acetone showed clearly the absence of the cyclopentadienyl peak whilst the peak at τ 2.65 (TMS as internal reference) may be assigned to the phenyl protons. The ionic nature of the complexes is further supported by their measured conductivities in nitromethane and acetone (Table I). The observed solid state magnetic moments of 4.1 and 4.0 B.M. of the chloride and bromide respectively (Gouy method) indicate some magnetic interaction between the two iron centres (in the solid state). Various byproducts were also produced in this reaction, thus, chromatography of the filtrate after isolation of the complexes [(DPCP)$_2$FeX] [FeX$_4$], X=Cl, Br, I, subsequent elution and purification gave (a) ferrocene in yields between 20-40%, (b) (η-C_5H_5)$_2$Fe(CO)$_2$ which exhibited ν(CO) bands at 2015 cm^{-1} and 1965 cm^{-1}

rates of substitution by phosphines and phosphites[1]. However, the presence of an intermediate with a ν(CO) band at 1969 cm^{-1} during the reaction suggests that halide substitution is probably the initial step with formation of [η-C_5H_5Fe(CO)$_2$-DPCP]$^+$ analogous to that observed initially in substitution of η-C_5H_5Fe(CO)$_2$N$_3$ by tertiary phosphites and phosphines[13]. Further substitution then occurs with displacement of the carbonyl group and finally reaction with a second unreacted substrate possibly via a radical mechanism gives the complex and (η-C_5H_5)$_2$Fe(CO)$_2$. The formation of the tetrahedral [FeX$_4$]$^-$ is probably due to its formation from FeX$_3$ produced in the reaction by radical decomposition of the substrate although the above scheme must be considered speculative at this stage.

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Chemistry Of Metal-Diene Complexes : ^{31}P NMR Studies of the Reaction of $(COD)PtCl_2$ with Tertiary Phosphines in Methanol≠

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Reactions of $(COD)PtCl_2$ with tertiary phosphine ligands in methanol have been studied by ^{31}P nmr spectroscopy. The formation of cationic complex $[(COD)PtClL]^+Cl^-$, ($L = Pr^i_3P$, Ph_2Bu^tP, Bu^t_2MeP, Cy_3P and Bu^n_3P) as the only product in the equimolar reaction between $(COD)PtCl_2$ and tertiary phosphines has been defined. In the reaction of $(COD)PtCl_2$ with two mole equivalent of tertiary phosphines, formation of various intermediate complexes including $[C_8H_{12}OCH_3)PtClL]$ by the nucleophillic attack of methoxyl-anion on the coordinated cyclo-octadiene has been observed.

IN transition metal catalysed organic synthesis, complex formation between a transition metal and an unsaturated organic molecule is considered to be an essential feature of the reaction. In view of this, various transition metal complexes with one or more weak donor ligands that can readily be displaced by the organic substrate, have been prepared. Cyclo-octadiene complexes of metals notably Rh and Ir have been widely utilized during recent years as catalysts towards organic substrates[1-5]. Cyclo-octadiene platinum complexes such as $(COD)PtCl_2$[6], $(COD)_2Pt$[7] (COD = cyclo-octadiene, C_8H_{12}) have also been used frequently for the synthesis of various complexes by ligand substitution[8-10]. Nucleophilic addition reactions with $(COD)PtCl_2$(1) have been studied in detail[11-13]. We have recently shown[14,15] that the methoxy addition product $[(C_8H_{12}OCH_3)MCl]_2$ (2) (M = Pt or Pd)) produces corresponding metal hydride complexes, *trans*-$MH(Cl)L_2$ when reacted with tertiary phosphine ligands in methanol. In continuation of our studies on metal-diene complexes, we report here the ^{31}P nmr studies of the reactions of tertiary phosphines with $(COD)PtCl_2$ (1) in methanol, which show the formation of cationic complexes $[(COD)Pt(Cl)L]^+Cl^-$ (3) by chloride substitution.

Experimental

Reactions were carried out under anaerobic conditions. Diethyl ether, pentane and hexane were dried and distilled over $LiAlH_4$. Methanol was dried and distilled over magnesium metal. Tricyclohexyl phosphine, Cy_3P, was obtained from its carbon disulfide adduct, $Cy_3P \cdot CS_2$, by heating in ethanol under nitrogen. Ph_2PCl, Bu^t_2PCl and Pr^i_3P (Strem Chemicals) were vacuum distilled prior to use. Tri-*t*-butylphosphine was prepared from the reaction of *t*-butyl lithium, with di-*t*-butyl chlorophosphine in hexane. Similarly, di-*t*-butyl methyl phosphine was prepared from the reaction of Bu^t_2PCl with methyllithium. Diphenyl *t*-butylphosphine was prepared from the reaction of Ph_2PCl with *t*-butyllithium. $(COD)PtCl_2$ was prepared from the reaction of excess 1,5-cyclooctadiene with K_2PtCl_4 in a mixture of propanol and water. A small amount of $SnCl_2$ was used as the catalyst in this reaction.

Proton and ^{31}P nmr spectra were recorded on Brucker 60 or 300 MHz Fourier Transform instrument. Deuterated-acetone or C_6D_6 was used as solvent with TMS as internal standard for the ^1H nmr spectra whereas ^{31}P nmr spectra were obtained in CH_3OH or C_6D_6 using H_3PO_4 as external reference. Microanalyses were performed by Atlantic Microlab, Atlanta, Georgia or M H W Microanalytical Lab, Phoenix, Arizona.

Reaction of (COD) $PtCl_2$ with tertiary phosphines in 1 : 1 molar ratio in methanol : When (COD)-$PtCl_2$, (1), was allowed to react with a tertiary phosphine in equimolar amount in methanol under nitrogen atmosphere and the reaction mixture was stirred magnetically at room temperature, a clear solution resulted within few min. ^{31}P NMR spectrum of this solution confirmed the reaction of phosphine with 1 forming a platinum-phosphine complex. Thus, ^{31}P nmr spectrum showed the disappearance of the starting phosphine signal and appearance of new signal associated with platinum

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≠ The authors of this work dedicate this contribution in honour of Professor R. C. Mehrotra on the occasion of his 60th birthday and in recognition of about four decades of distinguished service as a teacher and scientist.

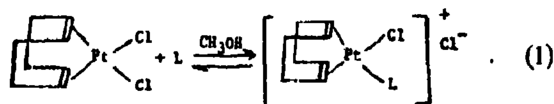
satellite. Typically, when Cy_3P (0.56 gm ; 2 mmol) was added to a magnetically stirred suspension of (COD)$PtCl_2$ (0.75 gm ; 2 mmol) in methanol (≈50ml) and the reaction mixture was stirred further at room temperature, a clear solution resulted within 30 min The reaction mixture was concentrated to a small volume (≈10 ml) *in vacuo* and a small fraction was syringed out and used for ^{31}P nmr spectrum. The spectrum showed a singlet at δ30.56 ppm associated with platinum satellites with JPtP -2859 Hz No other peak due to free phosphine was observed. Dropwise addition of benzene and hexane to the remaining solution resulted in the formation of yellowish-white crystalline solid This was filtered, washed with hexane and dried *in vacuo* (yield ~ 70%) Analytical and ^{31}P nmr data are given in Table 1.

In an attempt to isolate the complex 3 (L=Bu^t_3P) from a similar reaction of (COD)$PtCl_2$ with Bu^t_3P, when benzene and hexane were added to the clear solution, a white solid formed which was found to be starting (COD)$PtCl_2$ Anal Found : C, 25.9 ; H, 3.22 , Cl, 19.2% Calcd for $(C_8H_{12})_2PtCl_2$. C, 25.7 , H, 3.21 , Cl, 19.0%. The filtrate was found to contain free tri-*t*-butyl phosphine as analyzed by ^1H and ^{31}P nmr spectra

Reaction of (COD)$PtCl_2$ with R_3P in 1 2 molar ratio in methanol. Reaction of (COD)$PtCl_2$ with two mole equivalent of a tertiary phosphine results in a clear solution in methanol at room temperature ^{31}P NMR spectrum of this solution was found to be complex and consisted of signals due to various possible complexes (Table 2) Typically, when tricyclohexyl phosphine (0.56 gm , 2 mmol) was added to (COD)$PtCl_2$ (0.37 gm , 1 mmol) suspended in methanol (40 ml) under nitrogen atmosphere and the mixture was stirred at room temperature, a clear solution resulted within 20 min. The reaction mixture was concentrated *in vacuo* and ^{31}P nmr spectrum was recorded The spectrum showed several sets of signals explainable due to the formation of various complexes Upon addition of benzene/hexane to this solution, an off-white crystalline solid was isolated, which corresponded in analyses to $(Cy_3P)_2PtCl_2$ (yield ~ 65%) The filtrate was shown to contain 1,5-cyclooctadiene by gc/mass spec Analysis of solid ; Found C, 52.7 ; H, 8.02 ; Cl, 8.71 ; P, 7.42% Calcd for $C_{36}H_{66}Cl_2P_2Pt$: C, 52.3 , H, 7.99 , Cl 8.60 ; P, 7.51%

Results and Discussion

When a slurry of (COD)$PtCl_2$ (1) in methanol is reacted with an equimolar amount of tertiary phosphines such as Cy_3P, Ph_2Bu^tP, Pr^i_3P, Bu^t_3P, a clear solution resulted within a few minutes ^{31}P NMR spectrum of the solution showed only one set of signals consisting of a main peak associated with platinum satellites (Table 1), suggesting a coordination of the phosphine to the platinum From this reaction solution crystalline solid complex has been



(1)

isolated in the cases when L - Cy_3P, Bu^tPh_2P and Bu^t_2MeP and corresponded in analyses to 3 (Table 1) Proton nmr spectrum of complex 3 shows two sets of signals due to olefinic protons associated with platinum satellites suggesting the presence of non-equivalent *trans* groups In particular, a solution of 3(L Bu^t_2MeP) in d_6-acetone shows two sets of equally intense signals at δ6.20 ppm (JPt-H=43 Hz) and δ5.42 ppm (JPt-H 62Hz) Interestingly, the platinum phosphorus coupling constants (JPt-P)

TABLE 1– ^{31}P NMR SPECTRAL DATA AND THE ELEMENTAL ANALYSIS OF THE PRODUCT OF THE REACTION OF (COD)$PtCl_2$ WITH TERTIARY PHOSPHINE IN 1 1 RATIO IN METHANOL

S No.	Complex	δP (ppm)	J Pt P (Hz)	Analysis% Found (Calcd) C	H	Cl
1.	$[(COD)PtCl(PPh_2Bu^t)]^+Cl^-$	33.57	3054	46.3 (46.8)	5.07 (5.03)	11.9 (11.5)
2.	$[(COD)PtCl(PPr^i_3)]^+Cl^-$	42.52	2884			
3.	$[(COD)PtCl(PBu^t_2Me)]^+Cl$	22.05	2895	38.4 (38.2)	6.30 (6.18)	13.7 (13.3)
4	$[(COD)PtCl(PCy_3)]^+Cl^-$	30.56	2859	47.9 (47.7)	6.89 (6.88)	11.3 (10.9)
5	$[(COD)PtCl(PBu^t_3)]^+Cl^-$	77.10	2932			

TABLE 2—^{31}P NMR SPECTRAL DATA OF THE PROBABLE PRODUCTS OF THE REACTION OF (COD)$PtCl_2$ WITH TERTIARY PHOSPHINE IN 1 2 RATIO IN METHANOL

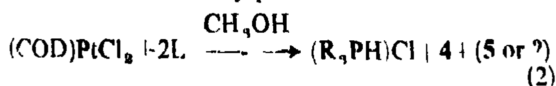
Complex 4	δ P (ppm)	JPtP (Hz)	Complex 5[a]	δ P (ppm)	JPtP
$[(C_8H_{12}OCH_3)PtCl(PPr^i_3)]$	36.39	3928	$[(C_8H_{12}(OCH_3)_2Pt(PPr^i_3)_2]$	28.75	1514
				30.86	1531
$[(C_8H_{12}OCH_3)PtCl(PBu^tPh_2)]$	39.10	4251	$[(C_8H_{12}(OCH_3)_2Pt(PBu^tPh_2)_2]$	33.47	1497
				34.58	1497
$[(C_8H_{12}OCH_3)PtCl(PBu^t_3)]$	69.96	3843			

a This may not be the actual complex

(JPtP=2859-3054Hz) (Table 1) observed for the complex 3 is found to be much smaller as compared to that of complex [$(C_8H_{12}OCH_3)Pt(Cl)L$], (4) (JPtP=3843-4251Hz), although in both complexes, the phosphine is *trans* to the olefinic carbon-carbon double bond. This implies that the Pt-P bond in complex 3 is weaker in comparison to that in 4. This is further supported by the fact that while complex 4 is quite stable in solvents like methanol, benzene, CH_2Cl_2 etc., complex 3 (when L=Bu^t_3P or Pr^i_3P) dissociates back into starting complex 1 and free phosphines in solvents such as benzene or hexane.

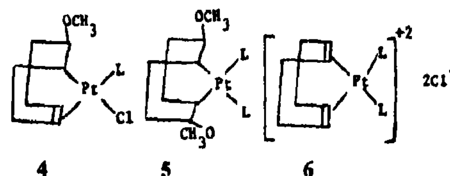
Thus the above reaction (eq 1) demonstrates that tertiary phosphine ligands, R_3P, have the ability to promote chloride substitution in protic solvents such as methanol, generating the corresponding cationic complexes, even in the absence of silver(I) salts. When the manuscript was under preparation, Hartley and coworkers[10] reported the preparation of some cationic complexes of the type $[M(LL)(Cl)L']^+ClO_4^-$ [M=Pt or Pd ; (LL)=$Ph_2PC_2H_4PPh_2$ or $Ph_2AsC_2H_4PPh_2$ and L'=tertiary phosphine] by chloride ligand displacement using silver(I) perchlorate. However, their attempts to displace chloride in the absence of silver(I) did not appear to succeed.

When an additional mole of the phosphine was added to the reaction (eq 1) containing complex 3 and the reaction mixture was examined by ^{31}P nmr spectroscopy, a change in the spectrum was observed. This showed the appearance of atleast three new sets of signals, none of which corresponded to free phosphine. A singlet with no platinum coupling was identified due to $(R_3PH)^+Cl^-$. A set of signals consisting of a main peak with large platinum-phosphorus coupling (JPtP≃4000 Hz) (Table 2) was found to be due to complex 4 which could be prepared independently by the bridge-splitting reaction of $[(C_8H_{12}OCH_3)PtCl]_2$ by appropriate phosphine[15]. Formation of complex 4 can be explained by the nucleophilic attack of methoxy anion on the coordinated diene[16] in the presence of phosphine as base. As a result of this $(R_3PH)Cl$ would be formed as by-product.



$$(COD)PtCl_2 + 2L \xrightarrow{CH_3OH} (R_3PH)Cl + 4 + (5 \text{ or } ?) \quad (2)$$

Besides these signals, another set of signals is also observed. This contains two main singlets associated with platinum satellites of much smaller magnitude (JPtP≃1500 Hz) (Table 2). Such small coupling constants are generally observed for phosphorus nuclei *trans* to O-bonded carbon in platinum(II) complexes[17] or tetravalent platinum-phosphine complexes[18]. The former statement is in favour of complex 5 which is a product of nucleophilic addition of two methoxy anions. Appearance of two singlets is probably a consequence of different stereochemistry (exo and endo) of the two methoxy groups on the cyclooctadiene, causing a non-equivalent *trans* group to the phosphines. When the methoxy-bridged dinuclear platinum complex $[(C_8H_{12}OCH_3)Pt(OCH_3)]_2$ obtained from the reaction of $(C_8H_{12})PtCl_2$ with sodium hydroxide, was allowed to react with 4 mole equivalent of Ph_3P,



complex 5 formed which showed a similar ^{31}P nmr spectrum. Proton nmr of this complex showed two types of methoxy signals at δ 2.88 and 3.09 ppm. Lewis and co-workers[20] have reported a similar reaction and have been able to isolate a complex $(C_8H_{12}acac_2)PtL_2$ (acac=acetylacetonyl) similar to 5.

Interestingly, when the solvent of the reaction (eq 2, L=Cy_3P) was removed and the residue was crystallized from CH_3OH/C_6H_6 hexane, crystals of $(Cy_3P)_2PtCl_2$ were obtained in ~70% yield, and free cyclooctadiene was isolated (by glc) from the organic phase. It is important to mention here that no insoluble solid was precipitated from methanol solution of this reaction even after keeping for over 2 weeks, suggesting the absence of any pre-formed $(Cy_3P)_2PtCl_2$ (7) before crystallization. Formation of complex (7) in the reaction might suggest a possibility of complex 6 in solution. However, such a complex should show a large platinum-phosphorus coupling constants (JPt-P≃3,000 - 4000 Hz) in the ^{31}P nmr spectrum. Since no such signals have been observed, the possibility of the existence of complex 6 in solution can be ruled out. Probably during the crystallization, attack of chloride ions on the complex 5 takes place to give the $(Cy_3P)_2PtCl_2$ complex[21]. Although, at present, we do not have any other evidence in favor of the above possible intermediate (5) efforts are being made to solve this problem.

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Studies on Rutaceae—Part III. Reactions and Rearrangements of Prenyl and Prenyloxy Coumarins

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During our study on the reactions and rearrangements of prenyl and prenyloxy coumarins interesting reactions and rearrangements were observed 7-Methoxy-8-(1', 2'-epoxy-3'-methylbut-3'-enyl)coumarin (phebalosin) (II) on oxidation with osmium tetroxide afforded 7-methoxy-coumarin-8-yl-acetaldehyde (XXXII) while 7-methoxy-8-(2'-hydroxy-3'-methylbut 3'-enyl) coumarin (auraptenol) (III) with *m*-chloroperbenzoic acid underwent rearrangement to 7-methoxy-8-(3'-formyl-but-2'-enyl) coumarin (XXX). The epoxy-lactone system of 7-methoxy-coumarin-6-(3', 4'-epoxy-3'-methyl)-γ-butyrolactone (micromelumin) (IV) opened up with boron tribromide to give 7-methoxy-coumarin-6-(3'-bromo-3'-methyl-4'-hydroxy)-γ-butyrolactone (XXXIII) while with 10% oxalic acid ring opening was accompanied by further degradation to give 6-formyl-7-methoxy coumarin (angelical) (XXXIV). Chromous chloride reduction of micromelumin (IV) afforded deoxymicromelumin (XXXVI) and oxidation with chromic acid/sulphuric acid degraded it to umbelliferone-methyl-ether-6-carboxylic acid (XXXVII). Dehydrogenation of dihydroseselin (VII) with DDQ resulted in an unusual product 3,6-dichloro-dihydroseselin (XXIV).

COUMARINS are widely distributed in the plant kingdom and are specially abundant in the families Umbelliferae and Rutaceae A vast majority of such compounds carry an oxygen function at C-7 and also bear isopentenyl side chain(s) These therefore offer the best example of a class of compounds exhibiting greater number of biogenetic modifications of the simple isoprenoid unit than any other class of natural products known today Various transformations with different reagents can be achieved involving these substituents resulting not only in the syntheses of coumarins already isolated from nature but also in the discovery of interesting reactions.

Experimental

The melting points were determined in a Kofler Block and are uncorrected The spectra were recorded. uv(λ_{max} in nm and log in parenthesis) on a Varian Techtron 634 in 95% aldehyde-free ethanol; ir (ν_{max} in cm^{-1}) on a Beckman IR-20 (KBr disc); pmr (chemical shift in δ, ppm) on Varian A-60D (60 MHz), CFT-20 (80 MHz) and XL-200(200 MHz) spectrometers ($CDCl_3$, d_6-DMSO; internal standard, TMS) Column chromatography and tlc were carried out with silica gel (60-120 mesh, BDH and 60-100 mesh, Gouri Chemical Works, Calcutta). The analytical samples were dried *in vacuo* over P_2O_5 for 24 hr. Anhydrous sodium sulphate was used for drying the organic extracts.

7-Methoxy-8-(3'-formylbut-2'-enyl) coumarin XXX) Auraptenol (III) (100 mg) was treated with *m*-chloroperbenzoic acid (80 mg) in dry chloroform at 0° under nitrogen atmosphere for 3hr Usual work up of the reaction mixture and chromatographic resolution on silica gel afforded XXX from benzene-ethyl acetate (9:1) eluate, m. p. 121-22° (petrol-benzene), yield 22%; uv (EtOH) 207, 217 and 321 (4 41 4 36 and 4 13), ir 1725 (formyl carbonyl), 1680 (lactone carbonyl intermolecular hydrogen bonding) and 1570, 1500 (aromatic) (Found: C, 69 70, H, 5 48 $C_{15}H_{14}O_4$ requires C, 69 76; H, 5.42%).

7-Methoxy-coumarin-6-(3'-bromo-3'-methyl-4'-hydroxy)-γ-butyrolactone (XXXIII): To a solution of micromelumin (IV) (100 mg) in anhydrous methylene chloride (10 ml) was added dropwise a solution of boron tribromide (0 4 ml) in methylene chloride (5 6 ml) The reaction mixture was stirred at 0-5° for 1 hr Usual work up of the reaction mixture and chromatographic resolution on silica gel afforded XXXIII from benzene-ethyl acetate (9:1) eluate, m. p 118-19° (benzene-ethyl acetate), yield 50%, uv (EtOH). 207, 223 and 323 5 (4 30, 4.21 and 4.13); ir 3380 (hydroxy), 1790 (5 membered lactone ring), 1730 (α, β-unsaturated lactone), 1630 ($>C=C<$) and 1570, 1505 (aromatic). (Found: C, 48 80; H, 3.60. $C_{15}H_{13}O_6Br$ requires C, 48.91; H, 3.53%).

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6-Formyl-7-methoxy coumarin (angelical) (XXXIV). Micromelumin (IV) (500 mg) in methanol (60 ml) was heated at reflux temperature with 10% oxalic acid (100 ml) and the distillate led into a solution of 2,4-dinitrophenyl hydrazine in aqueous hydrochloric acid. The water lost by evaporation was replaced at intervals from a dropping funnel. An orange 2,4-DNPH gradually separated from the 2,4-DNP solution and the distillation continued for 9-10 hr, until its formation became slow. The derivative was filtered, crystallized from rectified spirit as orange needles, m p 153-4°, yield 40%. It was shown to be identical with 2·4 DNPH of propionaldehyde (Found N, 23 35. $C_9H_{10}N_4O_4$ requires N, 23 5%.)

The non volatile part on extraction with chloroform, washing, drying and removal of solvent gave (XXXIV), m p 245-7° (ethyl acetate), yield 45%; (Found. C, 65 10; H, 3 99. $C_{11}H_8O_4$ requires C, 64 71; H, 3.92%)

Deoxymicromelumin (XXXVI). A solution of micromelumin (IV) (500 mg) in glacial acetic acid (50 ml) was added dropwise through a separating funnel to a solution of chromous chloride prepared from $CrCl_3$ (1 g) through which CO_2 was bubbled continuously. After complete addition the whole system was allowed to stand at room temperature in CO_2 atmosphere for 48 hr. The mixture was then diluted and extracted with chloroform. The chloroform layer on washing, drying and removal of solvent afforded XXXVI, m.p 204-5° (chloroform-methanol), yield 85%, uv (MeOH); 221,245,256 and 332 (4 22, 3 62, 3 55 and 4 20), ir: 1750 (γ-lactone carbonyl), 1730 (δ-lactone carbonyl) and 1620 (>C=C<). (Found: C, 66 99, H, 4 83. $C_{15}H_{12}O_6$ requires C, 66 18; H, 4 41%).

Umbelliferone-methylether-6-carboxylic acid (XXXVII). To a solution of micromelumin (IV) (190 mg) in 3% H_2SO_4 (38 ml) was added a solution of chromic acid (5 0 gm) in water (60 ml). The mixture was refluxed for 6 hr, cooled and extracted with ether (3×25 ml). The ether extract on washing, drying and removal of solvent afforded XXXVII, m p 250° (methanol), yield 56%, uv (EtOH). 207, 227 and 330 (4 16, 3 84 and 3 87), ir 3540 br(-OH), 1740 (lactone carbonyl), 1670 (carboxyl), 1120 (ether linkage) (Found C, 59 98, H, 3 71. $C_{11}H_8O_5$ requires C, 60.01; H, 3 63%)

7-Methoxy-coumarin 8-yl-acetaldehyde (XXXII): To a solution of phebalosin (II) (255 mg) in anhydrous benzene (10 ml) was added dropwise a solution of osmium tetroxide (250 mg) in benzene (10 ml) and pyridine (0 5 ml). The reaction mixture was stirred at room temperature for 24 hr. H_2S was then passed for osmate cleavage and osmium dioxide thus precipitated was removed by filtration. The filtrate on concentration and chromatographic resolution on silica gel column afforded XXXII in benzene-ethyl acetate (9:1) eluate, m p. 156° (white shining flakes from benzene), yield 20%, uv (EtOH): 211, 248, 257 and 323 (4 45, 3 84, 3.88 and 4.48); ir 1730 (formyl carbonyl and lactone carbonyl), 1610 (>C=C<) and 1570, 1500 (aromatic). (Found: C, 65 82, H, 4 62. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4 58%)

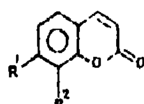
3,6-Dichlorodihydroseselin (XXIV). Dihydroseselin (VII) (100 mg) was dissolved in dry benzene (20 ml) and the solution was refluxed with DDQ (110 mg) for 50 min. The reaction mixture was cooled and dry HCl gas was passed through it for half an hr. The reaction was again refluxed for 1 hr. This process of refluxing and dry HClgas passing was continued until the time of refluxing became 32 hr. The coloured reaction mixture was separated from white hydroquinol, washed with 2% aqueous sodium bicarbonate solution, water and dried over anhydrous sodium sulphate. The benzene solution on concentration and chromatographic resolution on silica gel column afforded XXIV from petrol eluate, m p 163-5° (petrol), yield 54%; uv (EtOH) 231, 254, 265 and 343 (4 16, 3 65, 3 57 and 4 19). ir. 1720 (lactone carbonyl), 1605 (>C=C<) and 1580, 1460 (aromatic) (Found C,56 30 H,4 10. $C_{14}H_{12}O_3Cl_2$ requires C, 56 37, H, 4 02%)

Results and Discussion

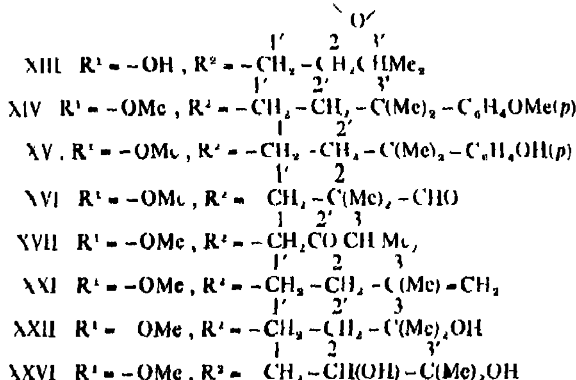
For our study we chose several naturally occurring coumarins bearing interesting and varied substitution patterns, viz., 7-methoxy-8-(3′-methylbut-2′-enyl) coumarin (osthol) (I), a major constituent of *Prangos pabularia* Lindl (Umbelliferae) and *Feronia limonia* Linn (Rutaceae), 7-methoxy-8-(1′,2-epoxy-3-methylbut-3-enyl) coumarin (phebalosin) (II) and 7-methoxy-8-(2-hydroxy-3′-methyl-but-3′-enyl) coumarin (auraptenol) (III), both occurring abundantly in *Murraya exotica* Linn (Rutaceae), 7-methoxy coumarin-6-(3′, 4′-epoxy-3′-methyl)-γ-butyrolactone (micromelumin) (IV), a major constituent of *Micromelum pubescens* Blume (Rutaceae) and 5-(2′,3′-epoxy-3′-methyl) *n*-butyloxy psoralen (oxypeucedanin) (V), another major component of *P pabularia*. In the course of our studies[1-4,7] on the chemical transformations of osthol (I) and its epoxide (VI) with various Lewis acids, unexpected reactions and rearrangements had been observed. This study was initiated with the object of elaborating easy routes to the pyrano- and furanocoumarins, dihydroseselin (VII), tetrahydrooroselone (VIII), dl-columbianetin (IX) and dl-lomatin (X), under mild conditions.

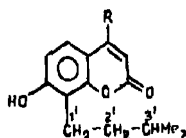
Friedel-Crafts reactions of I with toluene[1] and benzene[2] in the presence of anhydrous aluminium chloride resulted in arylation at C-4 with concommitant demethylation and disproportionation yiel-

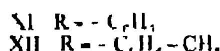
ding 3,4-dihydro-7-hydroxy-8-isopentyl-4-tolyl (XII) and 3,4-dihyro-7-hydroxy-8-isopentyl-4-phenyl (XI) coumarins in addition to 7-methoxy-8-isopentyl-coumarin (XIII). Under these reaction conditions it is apparent that the aryl radical attacks the benzylic site followed by disproportionation of the C_5-isopentenyl side chain and demethylation. However, in a later study[3] with anisole, arylation occurred at C-3′ giving rise to 7-methoxy-8-(3′-anisyl) isopentyl (XIV) and 7-methoxy-8-(3′-*p*-hydroxyphenyl) isopentyl (XV) coumarins in addition to XIII. The addition of the anisole moiety to the tertiary carbon at C-3′ is possibly due to its predominant anionic character, the anion being stabilised through its aluminium chloride complex.

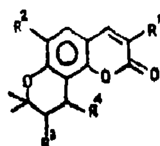


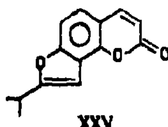


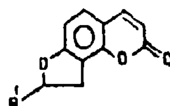


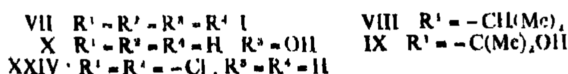




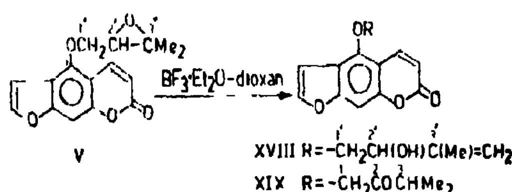








Boron trifluoride catalysed isomerisation, transformation and condensation reactions are well known. During our study of the rearrangements of prenyloxy coumarins with this reagent we were able to develop from osthol (I), via its epoxide (VI), an efficient synthesis[1,4] of 7-methoxy-8-(2′-formyl-2′-methyl-propyl) coumarin (XVI), a major lactonic constituent of *Citrus decumana* Linn (Rutaceae) in addition to the ketone, isoauraptene (XVII). The formation of the unusual product XVI can be rationalized to occur via a pinacol-pinacolone type of rearrangement involving the migration of the aryl part of the molecule to the incipient carbonium ion at C-3′. Isoauraptene (XVII) is produced by the migration of the hydride ion at C-2 to C-3′. Boron trifluoride has also been successfully used for the syntheses of two naturally occurring C-5 prenylated furocoumarins of *P pabularia*, 5-(2′-hydroxy-3′-methylene-*n*-butyloxy)-psoralen (pabulenol)[5] (XVIII) and 5-(2′-keto-3′-methyl-*n*-butyloxy)-psoralen (iso-oxypeucedanin) (XIX) by the rearrangement[6] of the epoxide, oxypeucedanin (V). With boron trifluoride phebalosin (II) rearranged[3] smoothly to 7-methoxy-8-(1′-formyl-2′-methyl-prop-1′-enyl)-coumarin (XX). The formation of this product possibly occurred via a pinacol-pinacolone type of rearrangement with migration of the aryl part of the molecule to C-2′. Investigation[7] of the reaction of osthol (I) with boron trifluoride resulted in the formation of its $\Delta^{3'}$-isomer (XXI). This contra-thermodynamic isomerisation appears to be interesting as the $\Delta^{2'}$-bond of osthol (I) migrates to a terminal position rather than to a conjugated site ($\Delta^{1'}$).



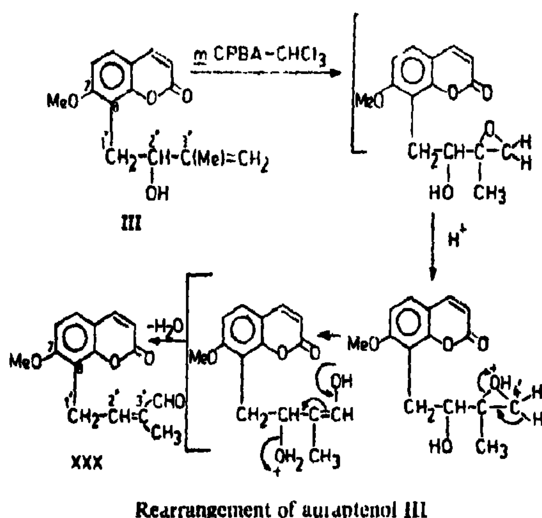
Synthesis of Pabulenol and Isooxypeucedanin

The use of boron tribromide as an effective demethylating agent is well known[8-12]. However, with osthol (I) and its epoxide (VI) different products were obtained depending on the molar concentration of the reagent[1]. With one mole equivalent of the reagent I yielded 7-methoxy-8-(3′-hydroxy-3′-methyl butyl) coumarin (XXII) while excess of the reagent brought about demethylation and cyclisation to dihydroseselin (VII). This on dehydrogenation would lead to seselin (XXIII). In a programme on the synthesis of angular pyrano- and furanocoumarins by functionalisation of the double bond in the pyran ring of XXIII we attempted a dehydrogenation reaction of VII, dissolved in dry benzene, with 2,3-dichloro-5,6-dicyanobenzoquinone under refluxing conditions. Instead of the expected compound XXIII we obtained XXIV. In the formation of compound XXIV apparently normal substitution took place at C_8 along with addition of chlorine at $\Delta^{3,4}$ followed by a dehydrohalogenation step.

Osthol epoxide (VI) with excess of boron tribromide was smoothly transformed[1] to dihydro-oroselone (XXV). With one mole equivalent of the reagent the major product was 7-methoxy-8-(2′-3′-dihydroxy-3′-methyl butyl)-coumarin (XXVI).

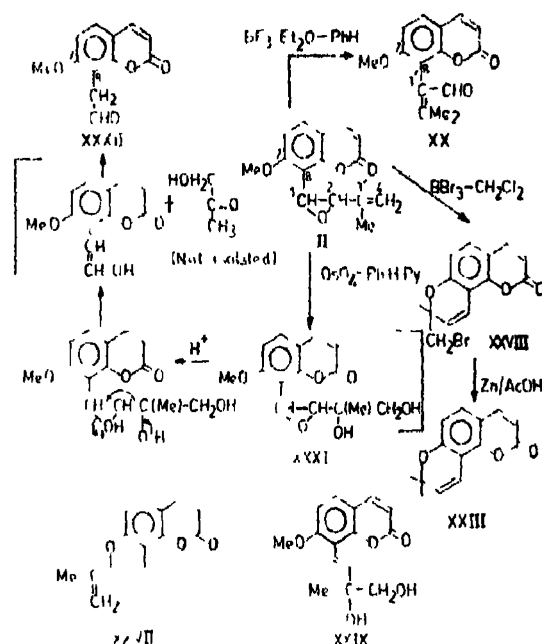
While using this reagent we had anticipated the demethylation of phebalosin (II) and subsequent cyclisation to oroselone (XXVII). However, II underwent an interesting rearrangement[8] to 2'bromoseselin (XXVIII) which on reduction with zinc and acetic acid afforded seselin (XXIII).

In a recent study directed towards the synthesis of casegravol[18] (XXIX) a naturally occuring coumarin of *Casearia graveolens* Dalz (Samydaceae) we contemplated the use of two starting materials, auraptenol (III) and phebalosin (II) The former on epoxidation followed by a dehydration step with subsequent ring opening of the oxirane function would directly lead to the coumarin XXIX. However, auraptenol (III) on treatment with *m*-chloroperbenzoic acid in chloroform at 0° under a nitrogen cover underwent rearrangement to 7-methoxy-8-(3'-formyl-but-2'-enyl) coumarin (XXX) This product must have been formed via the epoxide with subsequent removal of proton from C-4' and elimination of water. In the second approach we had intended to generate the vicinal glycol at C-3' and C-4' (XXXI) by treating II with osmium tetroxide followed by removal of the oxirane ring with triphenylphosphine to generate the olefinic linkage. However, oxidation with osmium tetroxide in dry benzene containing catalytic amount of pyridine resulted in the formation of 7-methoxy-coumarin-8-yl-acetaldehyde (XXXII) The latter is probably formed via the vicinal glycol (XXXI) followed by opening of the oxirane function and rupture of the C-2'- C-3' bond



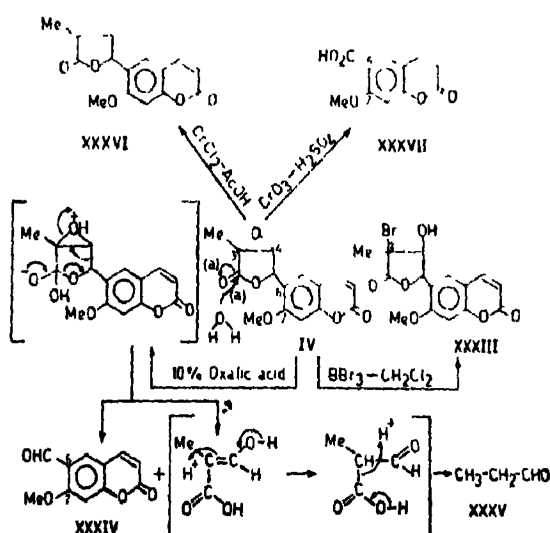
Rearrangement of auraptenol III

The presence of an epoxy-lactone system in the 5-carbon unit attached at C-6 in micromelumin (IV) offered an interesting system for study This was resistant to boron trifluoride The epoxy ring could, however be easily opened with boron tribromide in dry methylene chloride at 0-5° yielding 7-methoxy-coumarin-6-(3 bromo-3'-methyl-4'-hydroxy)-γ-butyrolactone (XXXIII). However on refluxing with 10% oxalic acid in methanol the epoxy ring opened up accompanied by further degradation to give



Reactions and rearrangement of phebalosin II

6-formyl-6-methoxy-coumarin (angelical) (XXXIV) in addition to propionaldehyde (XXXV) which was characterised as its 2,4-dinitrophenylhydrazone. The generation of a double bond with chromous chloride reduction is a characteristic reaction of an epoxy-lactone Micromelumin (IV) on treatment with chromous chloride in glacial acetic acid at 25° yielded 3',4'-deoxymicromelumin (XXXVI) On oxidation with chromic acid-sulphuric acid in water under reflux, it underwent degradation to umbelliferone-methyl ether-6-carboxylic acid (XXXVII) The identity of both the products, XXXIV and XXXVII, was established by comparison with authentic samples.



Reactions of micromelumin

The 80 MHz ^{1}H nmr spectrum in $CDCl_3$ of 3,6-dichlorodihydroseselin (XXIV), $C_{14}H_{12}O_3Cl_2$ (M^+ 298, 300 and 302) was highly significant. The coumarin C-4 proton resonated at 7 62 (1H, s) and the aromatic C-5 at 7.21 (1H, s). The two methyls at C-2′ of the pyran ring showed the characteristic six proton singlet at 1.36. The C-3′ and C-4′ methylenes appeared as triplets at 1.82 and 2 86 respectively (2H each, $J_1=J_2=7 0$ Hz) 7-Methoxy-8-(3′-formyl-but-2′-enyl) coumarin (XXX), $C_{15}H_{14}O_4$ (M^+ 258) showed in its 80 MHz ^{1}H nmr spectrum in $CDCl_3$ the characteristic coumarin doublets at 6 25 (C-3) and 7.66 (C-4) (1H, each J=9 5 Hz) and two aromatic *ortho*-protons at 7 37 (C-5) and 6 86 (C-6) (1H, d each J=8 0 Hz) The vinyl methyl resonated as a singlet at 1 95 (3H), the benzylic methylene at C-1′ as a doublet at 3 90 (2H, J=6 5 Hz) and the methoxy group (C-7) as a singlet at 3 95 (3H) The formyl proton exhibited a singlet at 9 36 The downfield one proton signal at 6 5 (t, $J_1=J_2=6.5$ Hz) was justifiably attributed to the vinyl methine at C-2′ which is in conjugation with the formyl group.

7-Methoxy-coumarin-8-yl - acetaldehyde (XXXII) $C_{12}H_{10}O_4$ (M^+218) showed in its 80 MHz ^{1}H nmr spectrum in $CDCl_3$ the characteristic coumarin doublets at 6 21 (C-3) and 7 63 (C-4) (1H each, J=9 0 Hz) and two aromatic *ortho* protons at 7 40 (C-5) and 6 85 (C-6) (1H, d each, J=8 0 Hz) The benzylic methylene (C-1′) appeared at 3 95 (2H, s) and the methoxy group at 3 88 (3H, s) The formyl proton resonated as a broad singlet at 9 72

The 200 MHz ^{1}H nmr spectrum in $CDCl_3$ of 7-methoxy - coumarin-6 - (3′ bromo - 3′ - methyl-4′ hydroxy)-γ-butyrolactone (XXXIII), $C_{15}H_{13}O_6Br$ (M^+ 368 and 370) showed the characteristic coumarin doublets at 6 33 (C-3) and 7.71 (C-4) (1H each, J=10 0 Hz) The C-8 and C-5 aromatic protons resonated as 1H singlets each at 6 89 and 7 53 (with finer splitting, J=1 0 Hz), the C-3′ methyl and C-7 methoxyl at 2 03 and 4 02 (3H s each) respectively

The benzylic methine (C-5′) appeared as a doublet with finer splitting at 5.53 ($J_1=4 0$, $J_2=1 0$ Hz) while the doublet at 4 86 (J=4 0 Hz) was attributed to C-4′ proton This fine splitting is possibly due to coupling with the aromatic proton at C-5 The singlet at 3 63 (disappearing on deuteration) is due to the hydroxyl at C-4′.

Deoxymicromelumin (XXXVI), $C_{15}H_{12}O_5$ (M^+ 272) showed in its 60 MHz ^{1}H nmr spectrum in d_6-DMSO the characteristic coumarin doublets at 6 14 (C-3) and 7 75 (C-4) (1H each, J=9 0 Hz) and two one proton singlets at 6 90 (C-8) and 7 32 (C-5) indicating their *para*-disposition In the aromatic region the one proton doublets each at 6.09 (J=4 0 Hz) and 7 38 (J=4 0 Hz) were attributed to the C-5′ and C-4′ protons respectively. The C-3′ methyl and C-7 methoxyl group resonated as singlets (3H each) at 1.85 and 3.90 respectively.

The structures of compounds (XXIV), (XXX), (XXXII) and (XXXIII) were further confirmed from their ^{13}C nmr data (Table 1).

TABLE—1 CARBON-13 NMR SIGNALS (δ) OF 3,6-DICHLORODIHYDROSESELIN (XXIV), 7-METHOXY-8-(3′-FORMYL-BUT-2′-ENYL)-COUMARIN (XXX), 7-METHOXY-COUMARIN-8-YL ACETALDEHYDE (XXXII) AND 7-METHOXY-COUMARIN-6-3′-BROMO-3′-METHYL-4′-HYDROXY-γ-BUTYROLACTONE (XXXIII) IN $CDCl_3$.

	XXIV	XXX	XXXII	XXXIII
C-2	154 20	160 80	160 95	160.0
C-3	118 40	113 28	113 31	114 0
C-4	138 70	143 62	143 27	143 0
C-4a	111 10	113 05	113 6	112 10
C-5	125 0	127 33	127 90	125 80
C-6	119 30	107 34	107 30	122 0
C-7	152 40	160 24	158 95	159 0
C-8	110 50	114 20	117 0	99 20
C-8a	149 70	152 94	153 50	155 80
C-7OCH$_3$		56 15	56 14	56 0
C-1′		22 78	37 72	
C-2′	76 5	150 75	197 45	173 10
C-3′	31 0	139 75		54 0
C-4′	16 8	9 25		81 0
C-5′				81 80
C-2′<CH$_3$ CH$_3$	26 30			
C-3 -CH$_3$				21 6
C-3′-CHO		195 50		

Acknowledgements

Sincere thanks are accorded to Dr A Patra, Dept of Pure Chemistry, Calcutta University for critical discussion and suggestions and to Sri A K Acharya Sri P Ghosh, Sri J Ghosh and Sri P. Pal of the Organic Instrumentation Laboratory, Dept. of Pure Chemistry, Calcutta University, for spectral measurements and to U.G C (India) and C C R A S (India), for financial assistance

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Infrared Spectroscopic Study of Saturation Extracts from Arid-Zone Field Soils Amended with Sewage Sludge+

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The surface horizons of two arid-zone field soils that had received amendments of composted, anaerobically-digested sewage sludge for four years were sampled to determine what changes may have occurred in the readily water-soluble fractions of the soils. Infrared spectra of evaporated films prepared from two-hour saturation extracts of the soil samples were interpreted to ascertain these changes. The ir spectra indicated that the majority of the compounds in the saturation extracts were carboxylates, carbonates, and nitrates, regardless of the rate of sludge application or the type of field soil. This result was considered to be an indication of substantial oxidation of the sludge organic compounds in the field soils, in agreement with the finding in a previous laboratory incubation study, that sludge decomposition would be rapid in an alkaline, unsaturated soil.

IN a recent study, Schaumberg *et al*[1] investigated the changes which occurred in the water-soluble fractions of sewage sludge soil mixtures that were incubated in the laboratory for 100 weeks. Infrared spectra of evaporated films prepared from saturation extracts of the sludge-soil mixtures showed that sludge decomposition followed a pattern which involved the disappearance of carbohydrate, protein, sulfonate and sulfate compounds, with the emergence of carboxylates and nitrates These transformations could be essentially complete in as little as 10 weeks, but were retarded considerably under acidic or water saturated conditions in the incubated soils

The question remains as to how these conclusions will apply to sludge decomposition under field conditions In this paper, that question is addressed through an infrared spectroscopic study of the readily water-soluble compounds extracted from the surface horizons of two arid-zone soils that had been used for about four years in field experiments conducted to assess the utility of anaerobically-digested sewage sludge as a soil amendment[2] The data obtained were expected to give information about the changes in the readily-soluble components of sludge in the soil environment

Materials and Methods

Soil samples · Surface horizons (0 15 cm) of two soils in randomized experimental plots located at the Moreno Field Station of the University of California, Riverside, were sampled in September 1979. The experimental plots were employed in a long-term field investigation by Chang *et al*[2] to ascertain the utility of anaerobically-digested sewage sludge as a soil amendment The plots sampled were fallow and had received composted sludge applications at the rate of 0, 10, 20 or 40 ton/acre (0, 22 5, 45 0 or 90.0 mT/ha). The composted sludge was obtained from the Joint Water Pollution Control Plant operated by the Los Angeles County Sanitation Districts

The composted sludge had been applied twice annually, beginning in the winter of 1975, to plots on Greenfield sandy loam (coarse-loamy, mixed, thermic Typic Haploxeralf) and on Domino loam (fine-loamy, mixed, thermic Xerollic Calciorthid). These plots had received eight sludge applications at the time they were sampled for the present study. During the period of sludge application, all of the field plots were cropped annually with barley (*Hordeum vulgare*) and sorghum (*Sorghum vulgare*). Complete details of the field experiments are given by Chang *et al*[2].

Some properties of the surface horizons of the two soils investigated are listed in Table 1. Detailed field observations and textural analyses indicated that soil properties were rather uniform across each experimental plot and throughout the upper 15 cm of the soil profile Chemical analyses showed that almost all (>90%) of the trace metal accumulation from sludge applications on the plots was in the upper 15 cm of the soil profile (Chang *et al*[3]). Accordingly, it was expected that studies of the surface soils in the plots would give significant information concerning changes in the applied sludge

+ Dedicated to Professor R C Mehrotra on the occasion of his sixtieth birthday

* Visiting Professor, Research Associate II, Professor of Soil Science, and Associate Professor of Agricultural Engineering, respectively Permanent address of the senior author is Dept of Chemistry, Sonoma State Univ , Rohnert Park, CA 94928.

TABLE 1—PROPERTIES OF THE FIELD SOILS (0-15 cm)

Soil	Particle size fractions% Sand	Silt	Clay	CEC meq/100g	Organic C %	$CaCO_3$ %	pH (sat paste)
Domino	42	35	23	14 0	4 3	1 2	7 8
Greenfield	62	27	11	8 7	0 8	0 0	7.1

Infrared spectral analysis : Saturation extracts of each soil sample were obtained in duplicate as described by Schaumberg *et al*[1]. Aliquots of the extracts were prepared for infrared spectral analysis also as discussed by these authors The ir spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer in the 4000 to 400 cm^{-1} wavenumber range Interpretation of the spectra was carried out with the assistance of standard references as listed by Schaumberg *et al*[1]. Principal band assignments are given in Table 2

TABLE 2—PRINCIPAL BAND ASSIGNMENTS IN THE IR SPECTRA OF THE SATURATION EXTRACTS

Band position cm^{-1}	Assignment
3400	OH, NH
1650–1550	COO
1430 1410	CO_3^{2-}
1430 1390	NH_4^+
1400 1310	COO, HCO_3
1380 1350	NO_3^-
1100 900	NH_4NO_3, $Ca(NO_3)_2$, Si-O
830 815	NO_3, HCO_3

Results and Discussion

The infrared spectra of the saturation extracts obtained from the field soils are reproduced in Fig 1 and 2. As in the study by Schaumberg *et al*[1] the ir spectra represent complex mixtures and are characterized by relatively broad bands Therefore, specific assignments must be regarded as not completely definitive However, several general conclusions can be drawn from an examination of the data

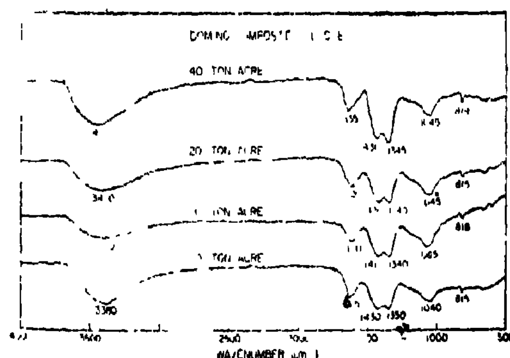


Fig. 1 The ir spectra of saturation extracts taken from the surface horizons of field plots on Domino loam The sludge application rate is shown with each spectrum.

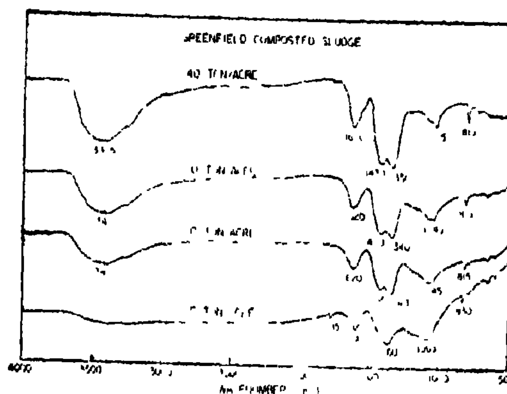


Fig 2 The ir spectra of saturation extracts taken from the surface horizons of field plots on Greenfield sandy loam The sludge application rate is shown with each spectrum.

For the most part, the ir spectra are dominated by bands which can be assigned either to inorganic compounds or to carboxylates Since sewage sludge is highly organic in nature, this result indicates that there has been a significant transformation of organic material to inorganic compounds (Cf Fig. 1 of Schaumberg *et al*[1]) All of the ir spectra of the saturation extracts from the treated field plots exhibit bands at about 3400 cm^{-1}, 1610-1635 cm^{-1}, 1415-1430 cm^{-1}, 1340-1360 cm^{-1}, 1040-1065 cm^{-1} and 815-830 cm^{-1} These bands may be assigned to OH and NH stretching modes ; carboxylate and water ; carbonate and ammonium ion ; nitrate, bicarbonate, and carboxylate ; nitrates and silicates (Si-O stretch) , and nitrate and bicarbonate, respectively The ir spectra of the extracts from the control plots (0 ton $acre^{-1}$) are quite similar to those of the extracts from the treated plots with the exception of the lack of a band at approximately 1420 cm^{-1} in the Greenfield saturation extract This band, if assigned to carbonate, would be expected to be absent, since the surface horizon of the Greenfield soil does not contain calcium carbonate (Table 1).

A comparison of the ir spectra for the two soils shows that spectra for plots receiving the same application rate of sludge are virtually identical Thus the spectra for Greenfield composted sludge at 40 ton $acre^{-1}$ and Domino composted sludge at 40 ton $acre^{-1}$ are almost superimposable The obvious conclusion to draw is that the differing characteristics of the soils have not affected dramatically the degradation pattern of the sludge Since the spectra for the control plots are somewhat different, it is apparent that, in the case of Greenfield soil, the application of the sludge has slightly altered the chemical characteristics of the soil Since the Greenfield soil is relatively low in organic carbon content (Table 1), and since the sludge is rich in organic material, this finding is not surprising

The ir spectra also show that, at least up to 40 ton acre^{-1}, the rate of sludge application does not appear to be critical in determining the compounds that appear during decomposition of the sludge. The nature and amount of readily water-soluble compounds in the soils receiving 10 ton acre^{-1} and those receiving 40 ton acre^{-1} appear to be similar

From a qualitative standpoint, the ir spectra obtained in this study are very similar to those obtained for an alkaline, unsaturated soil by Schaumberg *et al*[1] (Fig 1) at the end of their laboratory incubation study In both instances it appears as if a significant transformation to highly oxidized organic material or inorganic species has occurred The ir spectra obtained in the present study indicate that the rate of application of sludge has not altered significantly the composition of the readily water-extractable compounds in the two soils investigated although some changes were noted in the Greenfield soil

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Electron Spectroscopic Investigations of Carbon Monoxide, Nitrogen and Oxygen Adsorbed on Transition Metals+

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Carbon monoxide and nitrogen adsorb both molecularly and dissociatively on transition metals. Electron states of CO and N_2 molecularly adsorbed on metals have been studied by uv photoelectron spectroscopy. The bond order of adsorbed CO is between two and three both in the linear and bridged species. Oxygen dissociates on all metals except Pt, Ag and Au, the bond order of molecularly adsorbed oxygen on these metals being between 0.5 and 1.0. Electron states of molecularly adsorbed O_2 have been examined by uv photoelectron spectroscopy. The metal d orbitals donate electrons to the π^* orbitals of oxygen while the π orbital of oxygen donates electrons to the metal.

THE nature of bonding between adsorbed molecules and solid surfaces can be effectively investigated by employing techniques of electron spectroscopy. Thus, ultraviolet photoelectron spectroscopy (uvps) directly provides information on the molecular orbitals of the adsorbed species, while high resolution electron energy loss spectroscopy (HREELS) yields information on the vibrational frequencies of the adsorbed molecules. EELS employing high energy electrons is useful in obtaining information on the electronic transitions of the adsorbed molecules. Besides these techniques of electron spectroscopy, temperature programmed desorption (TPD) has been employed to identify the adsorbed species while LEED has been useful in determining the surface structure. In this article, we discuss the adsorption of three diatomic molecules, carbon monoxide, nitrogen and oxygen on transition metal surfaces as examined by electron spectroscopic techniques. It was our interest to obtain an unified understanding of the adsorption behaviour of these three molecules. While both carbon monoxide and nitrogen are known to adsorb on transition metals both molecularly (associatively) as well as dissociatively depending on the conditions and the metal, oxygen is almost always adsorbed dissociatively on metals. It is of importance to understand the nature of bonding between these molecules and metal surfaces since this information is of great relevance to catalysis and other surface phenomena.

Experimental

All the electron spectroscopic studies were carried out with an ESCA spectrometer of VG Scientific Ltd, U K, fitted with a sample preparation chamber and a gas handling manifold. Foils of transition metals of better than 99.9% purity were etched with argon ions under UHV coditions and it was ensured that the surface concentration of impurities like carbon and oxygen was negligible. Exposure of the metals to CO, N_2 and O_2 was made in the sample preparation chamber to the desired extent before the spectra were recorded. Exposures are referred to in langmuirs, L ($1L = 10^{-6}$ Torr sec). The temperature of the sample could be varied by using a special probe designed for the purpose.

Results and Discussions

Carbon monoxide. Carbon monoxide readily chemisorbs on all metals both dissociatively and molecularly[1-11], molecular adsorption occurs with a variety of geometries. In Fig 1 we show the molecular orbital diagram of carbon monoxide in free and adsorbed states. An examination of the molecular orbital picture tells us that the nonbonding 5σ orbital can be donated to the metal, while the empty $2\pi^*$ antibonding orbital can act as a potential recipient of electrons in the presence of a suitable donor like a metal. Fig 1 also gives us the picture of a carbon monoxide molecule sitting on a nickel atom. Such a donor-acceptor mechanism of bond formation[10] leads to important consequences. The 5σ level is stabilized as a consequence of bonding while the back bonding into the $2\pi^*$ level weakens the carbon-oxygen bond leading to a larger separation between the 1π and 4σ bonding orbitals. The net effect is to bring the 5σ and 1π orbitals of molecularly adsorbed carbon monoxide close to each other (see Fig 1). Since only valence orbitals are involved in this chemisorption phenomenon, we can employ ultraviolet photoelectron spectroscopy to characterize the adsorbed species.

We have carried out uvps studies of CO adsorbed on several transition metals. Fig. 2 gives the

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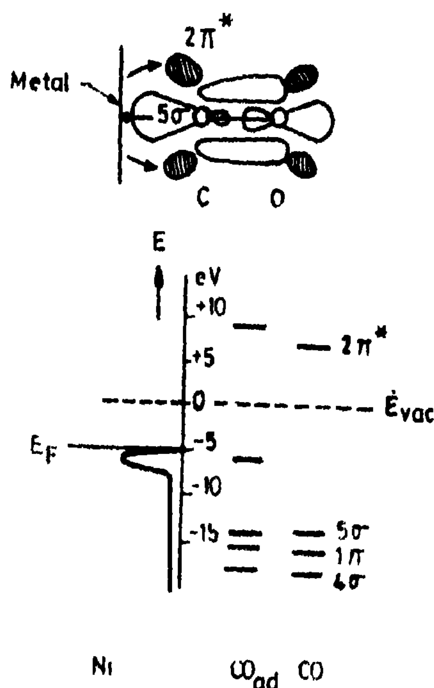


Fig 1. Mechanism of CO chemisorption on transition metals

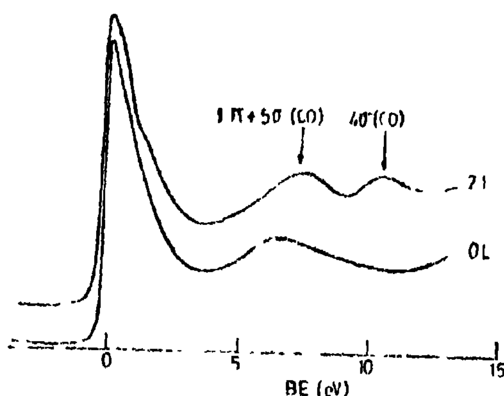


Fig. 2. Valence band of Ni exposed to CO at 300 K. The spectrum shows peaks due to molecular CO.

ultraviolet photoelectron spectrum of molecularly chemisorbed carbon monoxide on polycrystalline nickel We see two bands here at 7 5 eV and 11 0 eV The first band corresponds to the unresolvable (1π | 5σ) level of the adsorbed carbon monoxide, while the second is due to the 4σ level Angular distribution of photoelectrons has provided a basis for these assignments of bands in uvps[12] The binding energy of the 5σ orbital[13] is found to drastically vary with the heats of adsorption of carbon monoxide on different metals (Fig. 3) showing thereby that the stronger the metal-carbon bond, the greater is the stabilization of the 5σ orbital of the adsorbed molecule.

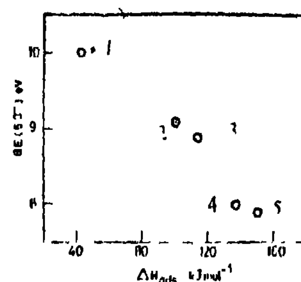


Fig 3 Variation of the binding energy of 5σ (CO) orbital with the heat of adsorption for CO chemisorbed on 1, Cu(311), 2, Pt(100), 3, W(100) and Ni(111), 4, Ni(110) and 5, Pd(100) and Ni(100)

EELS throws some light on the antibonding orbital of adsorbed carbon monoxide Although there is no direct method of measuring the $2\pi^*$ orbital energy of adsorbed molecules, EELS employing high energy electron beams, gives us the (5σ,$1\pi \to 2\pi^*$) excitation energy, E_T, since ultraviolet photoelectron spectroscopy gives us the 5σ binding energy, we can correlate the difference ($E_T - 5\sigma$), which is a good estimate of the π^* orbital energy, with the enthalpy of adsorption ΔH_{ads} (Fig 4) Interestingly, this plot parallels the variation in the metal $d \to 2\pi^*$(CO) charge transfer energy, which should also reflect the shifting of the π^* orbital on adsorption[14].

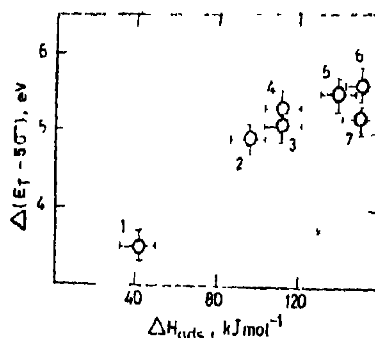


Fig 4. Relation between the π^* (CO) orbital energy and the heat of adsorption for CO adsorbed on metals (1) Cu(311), (2) Pt(111) and Pt(100), (3) W(100), (4) Ni(111), Ni(110), (6) Pd(100) and (7) Ni(100)

High resolution EELS employing low energy electrons throws light on the stereochemistry of the adsorbent-adsorbate system. In addition to giving the carbon-oxygen stretching frequencies, EELS also gives us the metal-carbon stretching frequencies and the subject has been reviewed extensively by Rao *et al*[15]. Specific ranges of carbon-oxygen stretching frequencies can be assigned to the different adsorption sites as can be seen from the assignments of Sheppard and Nguyen[16] given below :

$$1880-1650\ cm^{-1}\quad B_3(111)>B_4(100)>B_5(110)^*$$
$$2000-1880\ cm^{-1}\quad B_2(111)>B_2(100)>B_2(110)$$

2130–2000 cm^{-1} $C_8(111) > C_8(100)$
>2130 cm^{-1} oxidized metal surface

Here, B refers to a bridged site and C to a linear site. The subscript in the case of B stands for the number of atoms involved in bridging and subscripts in the case of C sites stand for the coordination of the metal atom.

In the case of linearly adsorbed carbon monoxide molecules, the carbon oxygen stretching frequency decreases as the metal-carbon stretching frequency increases as one would expect. The carbon-oxygen stretching frequency can also be related to the enthalpy of adsorption, ΔH_{ads} (Fig 5a). The carbon-oxygen stretching frequency falls as the heat of adsorption becomes more and more exothermic. We can relate the carbon-oxygen stretching frequency with the bond order as well (Fig 5b). From this correlation we see that linearly adsorbed carbon monoxide molecules have an average bond order close to 3.0 while those on the bridged B_2 site have a bond order closer to 2.4.

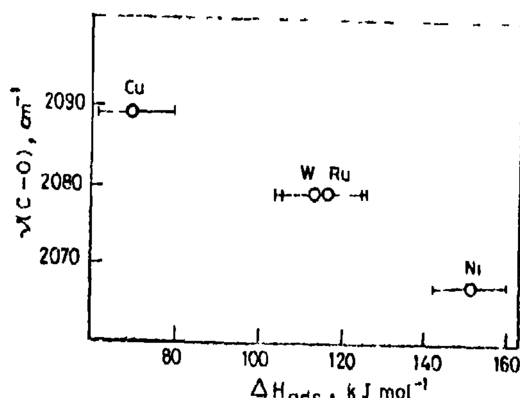
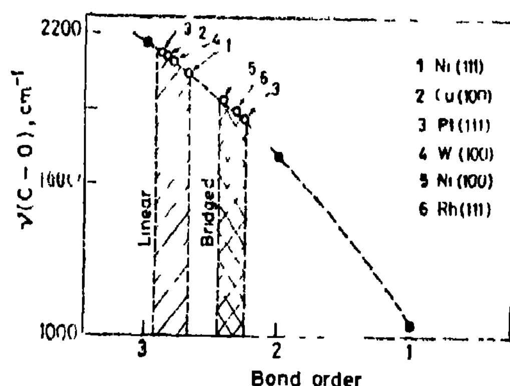


Fig 5 (a) Relation between C-O and the enthalpy of adsorption, ΔH_{ads} for CO adsorbed on transition metal (100) surfaces



5 (b) Variation of the carbon-oxygen (C-O) stretching frequency with the bond order. Regions for both bridged and linear species are indicated

According to Broden *et al*, transition metals to the left of the periodic table have a tendency to chemisorb carbon monoxide dissociatively, while the metals towards the right and bottom of the periodic table adsorb carbon monoxide in a molecular fashion[17]. Broden *et al* draw a borderline in the periodic table, to the left of which carbon monoxide is chemisorbed dissociatively, while it is molecularly chemisorbed towards the right. Such a classification, however, is far from comprehensive, as it explains chemisorption processes occuring at room temperature and low temperatures only. Adsorption at higher temperatures cannot be simply classified in this manner. Thus, cobalt and nickel, which lie to the right of this borderline, are found to dissociate carbon monoxide at higher temperature, around 400 K and Cu at 500 K[11]. Employing the enthalpy of adsorption ΔH_{ads} as a parameter, Benziger[18] has listed the enthalpies of dissociative and molecular chemisorptions of carbon monoxide on different metals, dissociative chemisorption becomes more and more exothermic towards the left of the periodic table, while towards the right and bottom, it becomes less and less exothermic, indeed it is endothermic (Fig 6). We would therefore expect metals towards the right to chemisorb carbon monoxide molecularly as their heats of molecular chemisorption are exothermic. Consideration of ΔH_{ads} alone, however, becomes untenable at higher temperatures, when entropy factors may outweigh enthalpy factors and a competition between the minimization of enthalpy and the maximization of entropy sets in. Such competetive factors determine a threshold temperature, above which dissociation sets in even though ΔH_{ads} forbids it[18]. Below the threshold temperature, dissociation is too slow. At this point we should note that the nature of chemisorption depends only on the electronic structure of the metal; the surface geometry of the adsorbent is relatively unimportant and becomes significant only in the case of metals close to the borderline.

Ti 577	V 410	Cr -335	Mn -279	Fe -136 (-105)	Co -90 (-103)	Ni -88 (-109)	Cu +21 (-71)
Zr 618	Nb 437	Mo 185	Te	Ru >0 (-124)	Rh >+19 (-130)	Pd >+25 (-147)	Ag +334 (-27)
Hf -667	Ta -469	W 215 (-88)	Re >-68 (-116)	Os >+12	Ir >+26 (-146)	Pt >+110 (-127)	Au >+164 (-58)

Fig 6 Enthalpies of dissociative and molecular (in parenthesis) chemisorption of carbon monoxide on different transition metals

In a recent study employing Auger electron spectroscopy[19], it has been found that carbon monoxide is dissociatively adsorbed on Ta, Nb and Ti but molecularly chemisorbed on Pd, Pt and Ir. We find that dissociated carbon monoxide shows XPS binding energies of C(1s) and O(1s) in the same range as those of metal carbides and oxides.

Under conditions of molecular adsorption, disproportionation of carbon monoxide, according to Boudouard reaction $2CO \rightarrow C + CO_2$, has been observed on transition metal surfaces[11]. Such a reaction leads to a larger build up of surface and subsurface carbon than a mere dissociation reaction would do. This carbon build up can be readily monitored by Auger and X-ray photoelectron spectroscopies. The carbon build up is quite understandable in the light of the reaction between the gas phase CO and adsorbed CO by the Eley-Rideal mechanism.

Nitrogen: Nitrogen is known to adsorb on transition metals both molecularly and dissociatively. The bonding scheme for molecularly adsorbed nitrogen is similar to that of carbon monoxide adsorption, the two molecules being isoelectronic. We took special interest in the study of nitrogen adsorption on Fe, as previous studies[19] on this system employed X-ray photoelectron spectroscopy only. UV photoelectron spectra of the previous studies invariably showed features due to carbon monoxide contamination. Fig 7 shows the uv photoelectron spectra of nitrogen and carbon monoxide on iron recorded by us. The spectra clearly bring out the differences between molecularly adsorbed nitrogen and carbon monoxide as can be seen from the table below

		5σ	1π	4σ
CO	free	14 0	16 8	19 7
	adsorbed	8 3	6 2	11 3
N_2	free	15 6	16 7	18 8
	adsorbed	8 0	6 5	11 0

UV photoelectron spectra upto 173 K clearly show three features at 6 5, 8 0 and 11 0 eV which can be clearly assigned to molecularly adsorbed nitrogen. The 6 5 and 8 0 eV peaks are due to $1\pi + 5\sigma$ levels, while the 11 0 eV peak is due to the 4σ level. Accompanying the development of these peaks in the valence region, we find that the intensity of the N(1s) signal in the X-ray photoelectron spectrum increases. The intensities of the C(1s) and O(1s) peaks are essentially constant during the adsorption of nitrogen suggesting that the peaks in the valence region are definitely due to nitrogen. Furthermore, the uv photoelectron spectroscopic bands of carbon monoxide adsorbed on iron (Fig 7) and recorded under similar conditions are found to be at different positions; in the case of carbon monoxide, we see a peak at 7 2 eV which is a composite band arising from 1π and 5σ levels; the second peak of carbon monoxide arises from the 4σ level.

Fig 8 shows the N(1s) bands in X-ray photoelectron spectra recorded during nitrogen adsorption on Fe for different exposures. Below 20L exposure at 80K, we see two peaks around 400 eV and 403-404 eV arising from two species of nitrogen-linear and bridged[20]. As we increase the temperature we see a peak appearing around 397 eV as can

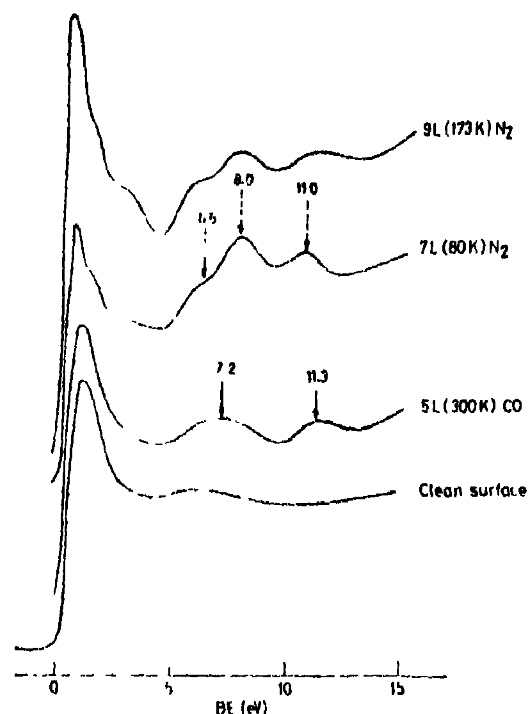


Fig. 7. [illegible] carbon monoxide [illegible] Fe

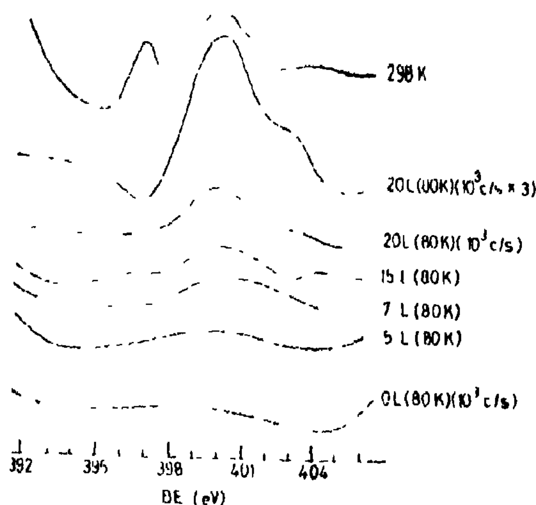


Fig. 8. N(1s) peaks in X-ray photoelectron spectra of the Fe + N system

be seen from the spectrum taken at 298 K. This is due to dissociated nitrogen. Nitrogen also, like carbon monoxide, is adsorbed dissociatively at high temperatures.

High resolution EELS of nitrogen adsorbed on W shows various loss peaks at 2120 cm^{-1} due to the nitrogen-nitrogen stretching frequency of the linear molecularly adsorbed species, 1440 cm^{-1} due to the nitrogen-nitrogen stretch of the nitrogen bridge bonded to two W atoms. The metal-nitrogen stretching frequencies for these two modes are seen at 480 cm^{-1} and 600 cm^{-1} respectively[21].

The nitrogen-nitrogen bond order in the linearly adsorbed species is slightly lower than that of molecular nitrogen, while the bridged species has a bond order close to 2

Although most transition metals are inert to adsorption of nitrogen, Broden *et al*[17] have proposed that those to the left of the periodic table have a tendency to dissociate the weakly held molecularly physisorbed γ states into the more strongly bound β states, which are thought to be the products of dissociative adsorption This is verified by soft X-ray appearance potential spectroscopy in which the low coverage N(1s) spectra on Ti and Cr resemble those of atomic nitrogen while the higher coverage N(1s) spectra resemble those of metal nitrides[22] Transition metals that lie to the right of the periodic table simply desorb the molecular γ states on heating[23] The same borderline as that drawn for carbon monoxide appears to hold good for nitrogen as well Benziger[18] has calculated the relevant enthalpies of adsorption (dissociative as well as molecular) and these data are depicted in Fig 9 to support the classification of nitrogen adsorption on transition metals

Ti -672	V -434	Cr -246	Mn -256	Fe -22	Co +16	Ni +2	Cu +148
Zr -730	Nb -510	Mo -138	Te	Ru <0	Rh > 0	Pd 0	Ag +510
Hf -738	Ta -542	W <-80	Re > 0	Os > 0	Ir > 0	Pt 0	Au >+54

Fig. 9 Enthalpies of dissociatively chemisorbed nitrogen on different transition metals

Oxygen : Unlike carbon monoxide and nitrogen discussed above, oxygen had been found to chemisorb only atomically on almost all metals until very recently[24,25] It was recently pointed out that molecular oxygen is stable at low temperatures (typically about 100 K) on silver and platinum surfaces In an attempt to base our conclusions on thermodynamic considerations, we calculated the enthalpy of dissociative adsorption of oxygen on different metals following the procedure of Benziger[18] We readily see that metals towards the left of the periodic table show larger exothermic heats of dissociative chemisorption (Fig. 10) The most striking feature is the fact that, while all metals at 298 K exhibit exothermic heats of dissociative adsorption (even Ag and Pt), only gold shows a positive heat of dissociative adsorption We have to come to the obvious conclusion that gold must adsorb oxygen molecularly at least at low temperatures These considerations tempted us to classify adsorption of oxygen on metals as in Fig 10

Ti -912	V -836	Cr -752	Mn -770	Fe 534	Co 478	Ni 486	Cu 326
Zr -1080	Nb 812	Mo 544	Te	Ru -220	Rh 162	Pd -170	Ag 62
Hf -1134	Ta 834	W 570	Re -356	Os 196	Ir 168	Pt	Au +54

Fig 10 Enthalpies of dissociatively chemisorbed oxygen on different transition metals

In order to investigate electron states of molecularly absorbed oxygen on metals and also to give credence to our classification in Fig 10, we have carried out low temperature uv photoelectron spectroscopic studies on oxygen adsorbed on silver and gold He II uv photoelectron spectra of clean and oxygen covered silver are shown in Fig 11 We see

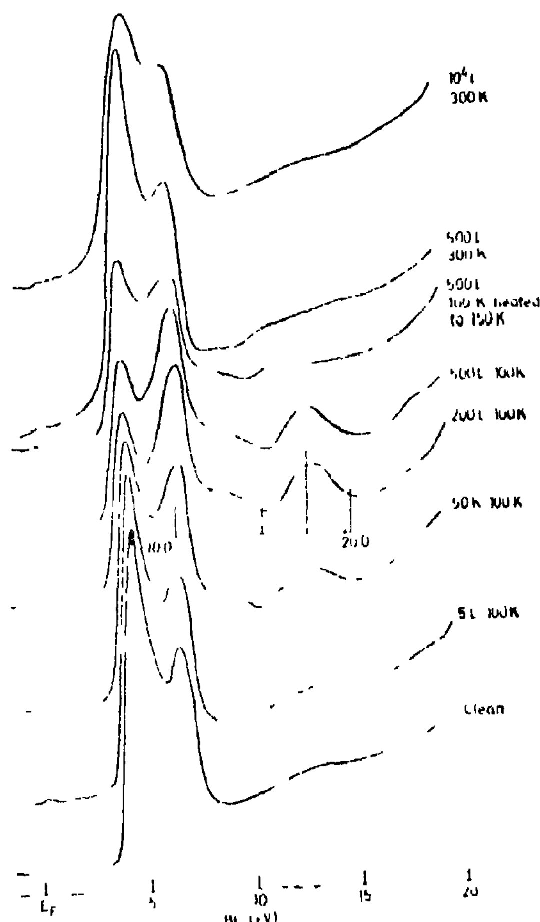


Fig 11 UV Photoelectron (He II) spectra of oxygen chemisorbed on polycrystalline silver Positions of bands in free O_2 are indicated by a bar diagram

peaks at 6 0 eV, 9 8 eV and a broad peak from 11 5-14 3 which compare well with the gas phase oxygen molecule Together with the development of these

peaks, we observed a large increase in the oxygen (1s) signal in the XPS (Fig 12) At lower exposures, we see a peak at 532 7 eV, which can be assigned to the molecular oxygen species. A lower binding energy peak at 531 7 eV is due to atomic oxygen due to initial dissociation of molecular oxygen. At higher temperature (300 K) we see only the lower binding energy peak at 529 7 eV due to chemisorbed atomic oxygen The molecular species has clearly desorbed

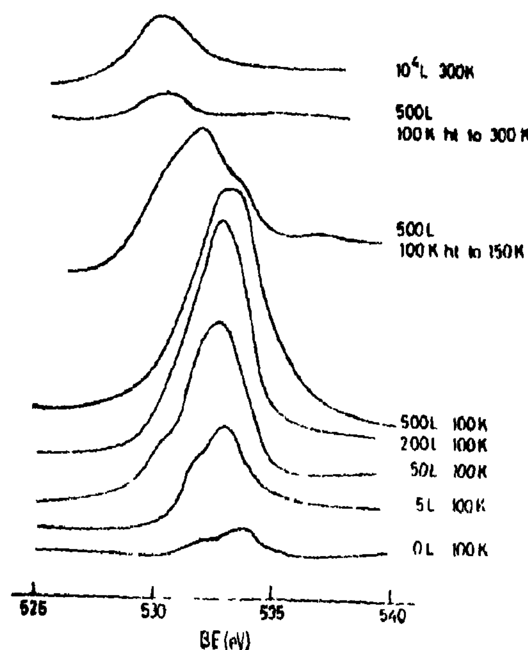


Fig 12 X-ray photoelectron spectra showing O(1s) bands for Ag+O_2 system

We have just completed preliminary uv photoelectron spectroscopic studies of oxygen adsorbed on gold and have established for the first time that oxygen can be molecularly adsorbed on gold at low temperatures (~150 K) On heating, the molecular species appears to desorb

High resolution EELS of molecular oxygen chemisorbed on metals[24,25] shows two vibrational frequencies at 240 cm^{-1} and 640 cm^{-1} in case of silver and 390 cm^{-1} and 870 cm^{-1} in case of platinum The lower vibrational frequency in both cases are due to the metal-oxygen stretch while the higher frequency is due to oxygen-oxygen stretch These low oxygen-oxygen stretching frequencies are clearly indicative of the weakening of the O-O bond on adsorption, partly due to donation of the metal electrons to the π^* orbitals of oxygen Based on the calculation of Backx *et al*[24], we can estimate (Fig 13) the population in the π^* orbital of the adsorbed oxygen to be 3 7 and 3 3 in the case of silver and platinum systems respectively. The oxygen-oxygen stretching frequency in the case of silver is much lower than that of a oxygen-oxygen single bond (as in peroxides) suggesting that there should be a mechanism for further lowering of the bond order

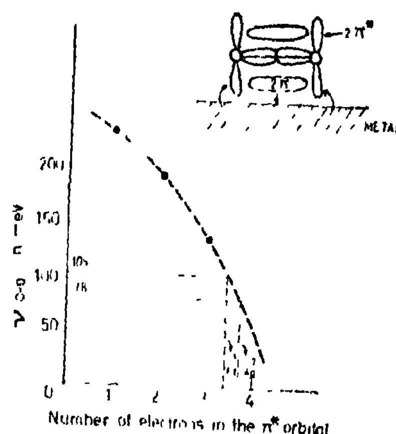


Fig. 13. Correlation of ν (O-O) stretching frequencies with the number of electrons in the π^* orbital MO diagram of O_2 adsorbed on metals is also shown

of oxygen besides that due to metal d→π^* charge transfer This can arise from donation of oxygen π electrons to the metal We can estimate the electron configuration of oxygen adsorbed on metals by considering the relationship between the oxygen-oxygen stretching frequencies and bond order (Fig 14) We see that the bond order in the case of silver is around 0 8 while it is 1 0 in the case of platinum Assuming that lowering of the oxygen-oxygen bond order from that of a single bond is due to donation of π electrons from oxygen to metal and taking the π^* population to be between 3 5 and 4.0 the electron configuration of oxygen adsorbed on transition metals can be written as $(\pi_u)^{3.5-4.0}(\pi^*_g)^{3.5-4.0}$.

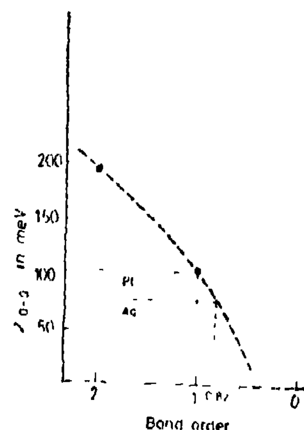


Fig. 14. Correlation of ν (O-O) stretching frequencies with the bond order

Temperature programmed desorption after oxygen adsorption on platinum at low temperatures shows two peaks, one at 150 K and the other at 800 K. The former is due to desorption of molecular oxygen, while the latter is due to desorption of atomic oxygen[26]. Clearly the low temperature molecular desorption is accompanied by atomisation. Indeed it is believed that molecular desorption sets in due to

atomisation. On atomisation, the atomic oxygen needs twice the number of sites than the molecular oxygen and hence a portion of the molecular oxygen desorbs. At low coverages, the presence of several empty sites causes a significant entropy factor to force dissociation at temperatures much lower than the temperature of molecular desorption. Putting these data together we can draw an imaginary phase diagram form the platinum-oxygen system (Fig 15). At low temperatures, we have molecular oxygen; but in addition, at low coverages, we have some atomic oxygen as well. Beyond a certain threshold temperature, dissociation sets in and only atomic oxygen can be found on the surface At still higher temperatures, we have the formation of bulk oxide layers.

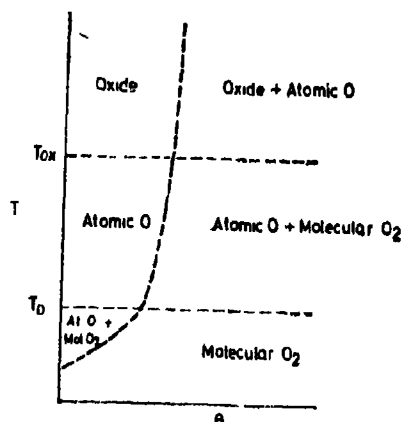


Fig. 15. Imaginer phase diagram of a Metal+O_2 system, plotted as a function of initial coverage.

Concluding remarks : Both carbon monoxide and nitrogen adsorb molecularly on surfaces of many transition metals and undergo dissociation on certain metals. The tendency to dissociate can be rationalized on the basis of the enthalpies of adsorption. When these molecules adsorb molecularly, the bond order falls to a value between 2 0 and 3 0.

Unlike carbon monoxide and nitrogen, oxygen adsorbs on transition metals almost always dissociatively and where the thermodynamics of dissociative adsorption is unfavourable, it adsorbs molecularly at low temperatures, Pt, Ag and Au being the only three such metals. Molecularly adsorbed oxygen is associated with a bond order between 0 5 and 1 0.

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Dioxygen Complexes of the Heavier 4d and 5d Transition Metal Ions*

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Dioxygen complexes of the heavier transition metal ions of the 4d and 5d series are in general more stable than those of the 3d series and many of the complexes can be isolated and studied In most of these complexes dioxygen is coordinated in an edge-on "dihapto" fashion Vaska's complex $IrCl(CO)(PPh_3)_2(O_2)$ has been the most well studied complex in this series and was the first to be isolated.

New end-on complexes of Ru(III) with triphenylarsine and water soluble complexes with EDTA and HEDTA have been prepared and characterized Besides the Co(II)-dioxygen carrier which are quite well known, the ruthenium(III)-dioxygen complexes are the only examples of reversible coordination of dioxygen aqueous solution.

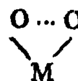
DIOXYGEN complexes of transition metal ions have gained much importance in recent years because of their oxygen transport and their participation in oxidation reactions[1]. Dioxygen complexes are defined as those complexes in which two oxygen atoms are bonded together and are also coordinated to one or two metal ions. These complexes are formed either by the direct coordination of dioxygen to a metal ion in a low oxidation state followed by charge transfer to and from dioxygen to the metal ion or by the direct interaction of H_2O_2 or superoxide ion with a metal ion in a higher oxidation state. The two routes, however, give rise to the same type of complexes[2] and in many cases their formation involves a reversible coordination of dioxygen to the metal ion from which either dioxygen or H_2O_2 can be generated under suitable conditions and electron shift reactions The charge transfer from the metal ion to the dioxygen moiety may vary from a small extent as in oxyhaemoglobin[3] to the formation of a formal superoxide, O_2^-, or peroxide, O_2^{2-}, anions by the transfer of one or two electrons to O_2, respectively. The extent of charge transfer to dioxygen in a given complex is computed mainly on the basis of the O^{17} hyperfine splitting of the epr signal in dioxygen complexes.

The existence of dioxygen complexes in biological systems was first recognized when oxyhaemoglobin, the carrier of O_2 in vertebrates blood was characterized[3] as a 1:1 Fe(II)-dioxygen complex The bent end-on coordination of dioxygen to the Fe(II) ion in oxyhaemoglobin was postulated by Pauling[3] in 1936 and confirmed by the X-ray structure of the complex by Phillips[4] in 1978 Decammine-μ-peroxodicobalt(III) ion, $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ was the first synthetic dioxygen complex which was thoroughly characterized by Werner[5] in 1898 In subsequent years, Werner and his group[6] isolated several -μ-peroxo and double bridged -μ-peroxo-μ-hydroxo or imido double bridged complexes of Co(III) The practical applications of synthetic oxygen carriers started around 1940 when Calvin and his coworkers[7] demonstrated the oxygen absorption and desorption properties of the Co(II) Schiff's base complex, *bis*-salicylaldehydeethylenidiiminecobalt(II), 'Salcomine'. In subsequent years work on Co(II)-dioxygen carriers in solution was done by a group of investigators[8,9] notably by Martell and coworkers[10,11]. In the last decade notable contribution to metal-dioxygen chemistry was made by Basolo and coworkers[12] who worked on manganese-porphyrinatodioxygen complexes and Collman and his group[13] who synthesized sterically protected Fe(II) porphyrin complex that acts as haemoglobin model[14].

Work on the dioxygen complexes of heavier transition elements of the 4d and 5d series made its beginning after the discovery of chlorocarbonyl*bis*-(biphenylphosphine)iridium(II)dioxygen complex, $IrCl(CO)(PPh_3)_2(O_2)$ by Vaska[15] in 1965. Since the discovery of Vaska's complex, about hundred dioxygen complex of 4d and 5d transition elements were prepared and the structure of about forty of these complexes is now known[1] The present article will be confined to these complexes. Excellant reviews[11,12] deal with the dioxygen complexes of the 3d transition metal ions The classification of the complexes discussed is based on the type of coordinated dioxygen to metal ion.

I. *1:1 η^2-Peroxo complexes* :

The term dihapto η^2-peroxo is used in this article for edge-on coordinated complexes of dioxygen where both the ends of oxygen are considered to be coordinated to a single metal ion



In the 4d and 5d series of transition elements such complexes are formed by two routes : a direct interaction of metal ions in $M^{+1}(d^8)$ or $M^0(d^{10})$ configuration with dioxygen and the subsequent formation of $M^{+3}(d^6)(O_2^{2-})$ or $M^{+2}(d^8)(O_2^{2-})$ complexes, respectively Such reactions may be broadly considered to be oxidative addition reactions of dioxygen with the metal ion Reaction of $M^{+6}(d^0)$ metal ions with H_2O_2 in the presence of suitable ligands also give rise to the η^2-peroxo complexes Most of the peroxo complexes of group V and group VI transition metal ions like Nb(V), Ta(V), Mo(VI) and W(VI) were obtained by this route[16]

a) *Dioxygen complexes of nd[8] elements, Rh(I), Ir(I)* :

Extensive work on Vaska's complex has been done in regard to its structure[17] which shows a dihapto coordination of dioxygen to the metal ion.

* Dedicated to Prof. R. C. Mehrotra ; teacher, friend, philosopher and scientist, on the occasion of his sixtieth birthday.

The ir spectra of this complex and other η^2-peroxo complexes give peaks around 840-870 cm^{-1} indicating the presence of a coordinated peroxo group in the complex. Dioxygen is reversibly coordinated in the complex $IrCl(CO)(PPh_3)_2$. The oxygen absorption and desorption studies have indicated that the coordinates of dioxygen to the metal ion is accompanied by a favourable enthalpy (12 to 13 e u) and large negative entropy (-22 to -24 e u change which is characteristic of an oxidative addition reaction involving a polar transition state Various analogues of Vaska's complex were prepared[1] by the variation of the anionic group from Cl^- to F^-, Br^-, I^-, CN^-, NO_3^-, $RC{=}C^-$, $C_6H_5^-$, $XC_6H_4^-$ and the π-acidic triphenylphosphine ligand to various aralykyl phosphines and arsines. Neutral iridium(I) dioxygen complexes in the absence of CO are relatively unstable. Thus, the complex $IrCl(O)_2(PPh_3)_2$ is very poorly characterized[18].

The rhodium(I) analogue of Vaska's complex $Rh(CO)Cl(PPh_3)_2$ does not react[19] with O_2, indicating that the presence of highly π-acidic ligands like CO is not essential for the dioxygen complex formation in the 4d series. Mild π-acidic ligands like isonitriles can stabilize[20] the rhodium(I) dioxygen complexes of the type $RhCl(O_2)(PPh_3)_2(RNC)$ (R = *t*-Bu, C_6H_{11}, *p*-$CH_3C_6H_4$) Unlike Ir(I), rhodium(I) gives very stable[21] dioxygen complexes of the type $RhCl(O_2)(L)_3$ (L=PPh_3, $AsPh_3$)

Stable cationic dioxygen complexes of Rh(I) and Ir(I) of the composition $ML_4(O_2)A$, [M=Rh(I), Ir(I), L=PMe_2Ph, $AsMe_2Ph$, A=BPh_4^-, BF_4^-] were isolated and characterized[21,22] Polydentate phosphines also yield stable dioxygen complexes with Rh(I) and Ir(I) The Rh(I) dioxygen complexes of polydentate phosphines are more stable than the monodentate phosphines.

Bis-1,2-diphenylphosphinoethane (diphos) gives stable[23,24] complexes of the type $M(diphos)_2(O_2)A$ with Rh(I) and Ir(I) Taqui Khan and Martell[25] reported the cationic dioxygen complexes of Rh(I) and Ir(I) of the composition $RhL(O_2)Cl$ with tetradentate phosphines, tetraphos-1($\phi_2PCH_2CH_2P\phi CH_2CH_2P\phi CH_2CH_2P\phi_2$) and tetraphos-2,-$P(CH_2CH_2P\phi_2)_3$. The yellow orange dioxygen complexes are very stable in solution and in the solid state. Novel *bis*-dioxygen complexes of the hexaligate bimetallic ligands, TDDX and TDADX of the composition $M_2(TDDX)Cl_2(O_2)_2$ [M=Ir(I), Rh(I)] and $Rh_2(TDADX)Cl_2(O_2)_2$ were reported by Taqui Khan *et al*[26,27]. These novel complexes have dioxygen coordinated to each metal centre in the binuclear complex (Fig 1) These binuclear complexes are models for surface activation of molecular oxygen where more than one metal centre is involved in complexation with the diatomic molecule.

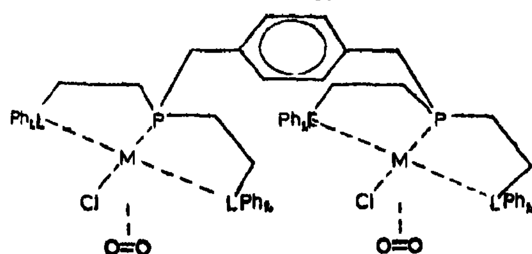


Fig. 1. L=P, (TDDX), L=As(TDADX)

b) *Dioxygen complexes of nd⁸ elements Ru⁰ and Os⁰* :

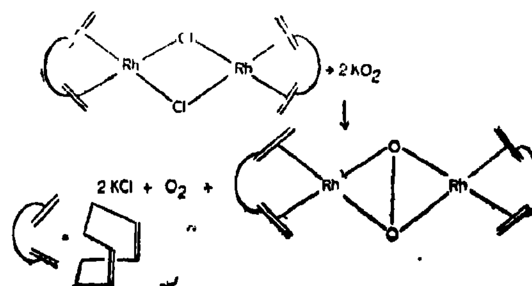
4d⁸ complexes of Ru⁰ formally stabilized by NO or CO groups react with dioxygen to form well characterized dioxygen complexes. Brown diamagnetic dioxygen complexes of the composition $RuX(NO)(O_2)(PPh_3)_2$ ($X{-}Cl^-$, Br^-, I^-, OH^-, NCS^-, NCO^-, CN^-, N_3^-, NO_3^-) were isolated[28] by the oxygenation of the complexes, $RuX(NO)(PPh_3)_2$ in the solid state and in solution. Examples of Rh⁰ and Os⁰ dioxygen complexes stabilized[29] by CO are $M(CO)_2(PPh_3)_2(O_2)$ Dioxygen reacts with the four coordinate nd⁸ complexes $M(CO)_2(PPh_3)_2$ to form the six coordinate formal Ru(II) or Os(II) complexes of the composition $M(CO)_2(O_2)(PPh_3)_2$ The Os(II) complex, $Os(CO)_2(O_2)(PPh_3)_2$ is the only example of an osmium-dioxygen complex reported so far.

c) *Dioxygen complex of the nd¹⁰ elements Pd⁰ and Pt⁰* :

Wilke *et al*[30] reported dioxygen complexes of Pd(O) and Pt(O) of the composition $M(PPh_3)_2(O_2)$ [M=Pd(II), Pt(II)] by the oxygenation of $M(PPh_3)_4$ in dry benzene. The platinum(II) complex is more stable than the Pd(II) complex which is the order of stability expected for the complexes of transition metals 5d>4d>3d Hydride[31] elimination from $PtH_2(PR_3)$, (R = C_6H_{11}, ipr) by CO in the presence of air resulted in the formation of the dioxygen complexes $Pt(O_2)(PR_3)_2$ admixed with $Pt(CO_3)(PR_3)_2$ The latter complex is formed by the oxidation of CO to CO_3^{2-} within the coordination sphere of the metal ion in the complex $Pt(O_2)(PR_3)_2$ The Pd(O) complex $Pd(t\text{-}BuNC)_4$ reacts[32] with O_2 in benzene to form the dioxygen complex $Pd(O_2)(t\text{-}BuNC)_2$ The dioxygen complexes of Pd(O) and Pt(O) are very reactive and take part in oxygen atom transfer reactions.

II 2 1 *Dihapto-μ-peroxo complexes* :

Suzuki *et al*[33,34] isolated dihapto-μ-peroxo complexes of Rh(I) of the composition $Rh_2(dien)_2O_2$ (dien=cycloocta-1,5 diene), by the reaction of the

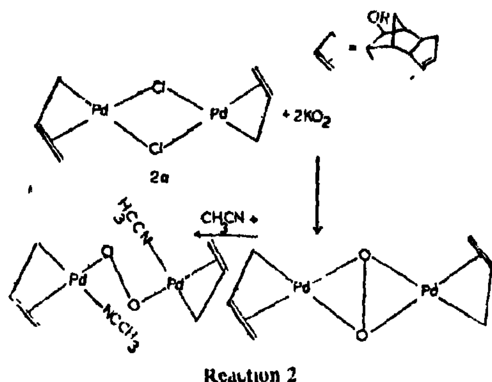


Reaction 1

bridged complex $M_2(dien)_2Cl_2$ with KO_2 in CH_2Cl_2 (Reaction 1).

The reaction may be visualized as the replacement of the chloro bridged anions by the peroxo group obtained by the autooxidation of two molecules of KO_2.

In the case of Pd(II) the reaction[34] of the chloro bridged organometallic Pd(II) complex[2a] with KO_2 in CH_2Cl_2 gives the dihapto-μ-peroxo complex of Pd(II)[3b] (Reaction 2).



Reaction 2

The dihapto-μ-peroxo Pd(II) complex 2b reacts with CH_3CN to give the μ-peroxo Pd(II) complex 2c. Reaction 2 in an interesting case of the conversion of a dihapto-μ-peroxo complex to a bent-end-on-μ-peroxo species.

III. *2 : 1 Bis-dihaptoperoxo complex* :

A novel binuclear *bis*-dihapto complex of Rh(I) of the composition $[RhCl(O_2)(PPh_3)_2]_2$ was obtained by Bennett and Donaldson[35] by the oxygenation of $RhCl(PPh_3)_3$ in benzene solution The structure of the dimeric complex can be represented in terms of a trigonal bipyramidal coordination of two rhodium atoms. The complex may best be described as a *bis*-dihapto-μ-peroxo complex where one of the peroxo oxygens binds two formal rhodium(III) ions through two ion pairs while the other oxygen atom is coordinated in a monohapto manner to only one Rh(III) ion (Fig. 2).

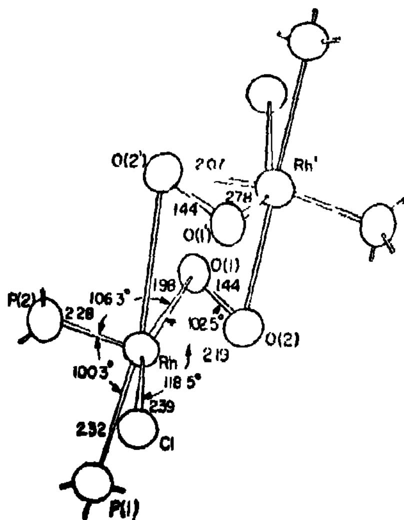


Fig. 2

IV. *1 : 1 Superoxo and 1:2-μ-superoxo complexes of Rh(III)* :

The 1 : 1-μ-peroxo complexes of 4d and 5d transition elements are rather less known and have started to be recognized recently. These complexes are formed by metal ions in a comparitively higher oxidation state Cillard *et al*[34] have reported a 1:1 superoxo complex of Rh(III) of the composition $[Rh(en)_2(NO_2)(O_2^-)]^+$ by exposing a solution of $[Rh(en)_2(NO_2)_2]^+$ to sunlight in the presence of O_2. The complex exhibits a strong Raman band at 1052 cm^{-1} characteristic of a superoxo group

In the presence of aquorhodium(III), the red monomeric superoxo complex is converted to the blue or purple dimeric species, $[X(en)_2RhO_2Rh(en)_2X]^{m+}$($X=Cl^-$ or H_2O). The complexes are paramagnetic and are the counterparts of the 3d^6 superoxo complexes of Co(III) which are very well known

V *1 : 1-μ-Peroxo complexes of Ru(IV)* .

The binuclear peroxo complexes of the (4d^6) Ru(IV) ion have been recently reported by Taqui Khan and Veera Reddy[36] and Taqui Khan and Ramchandraiah[37]. A solution of $RuCl_3(AsPh_3)_3$ reacts with O_2 in benzene solution to form the -μ-peroxo complex, $[(AsPh_3)_2Cl_2RuO_2RuCl_2(AsPh_3)_3]Cl_2$ The complex is paramagnetic with the μ_{eff} value corresponding to two unpaired electrons per ruthenium ion, supporting a spin paired Ru(IV) configuration for the metal ion The νO_2 frequency in the complex is observed at 845 cm^{-1}corresponding to a coordinated peroxo species The presence of a peroxo group in the complex is also supported by the photoelectron spectrum of the dioxygen complexs which shows a peak at 532 eV corresponding to a peroxide group The 4d5/2 photoelectron peak indicates that arsenic is in a tervalent state thus ruling out the 845 cm^{-1} stretch as due to νAs–O. The electronic spectrum of the complex exhibits spin allowed bands at 520 nm (E=1696) and 410 nm (E=4162) which may be assigned to $3T_1 \rightarrow 3T_2$ and $3T_1 \rightarrow 3E$ transitions respectively in a distorted octahedron. There is

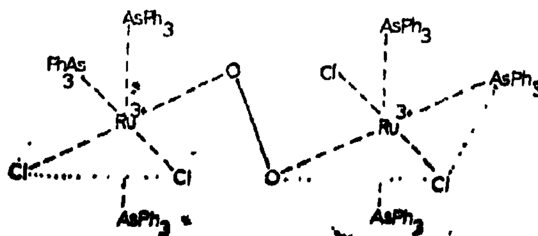


Fig. 3

also an intense band observed at 380 nm involving the L→M charge transfer for the peroxo group. The complex has been assigned the structure as shown in Fig. 3.

Taqui Khan and Ramchandraiah have recently reported[37] the dioxygen complexes of Ru(II) in aqueous solution with EDTA and HEDTA. A 1:1 solution of $RuCl_4$-EDTA and HEDTA, when titrated with a base in the presence of dioxygen indicate the formation of -μ-peroxo-μ-hydroxo complexes. The $\log K \frac{M_2L_2H_2O_2O_2}{(ML)_2(O_2)(OH)}$ values for L-EDTA and HEDTA complexes are 29 8 ± 0.2 and 22 1 ± 0 2 respectively. By the gas absorption measurements the number of oxygen molecules bound to the metal chelate were found to be one mole per two moles of the metal complex. Conductivity data on the aqueous solution of the complexes indicate that they are 3 : 1 electrolytes. The O_2 of the coordinated peroxo group in the complexes are at 897 cm^{-1}. The coordinated peroxo group can be displaced from the complexes by the addition of a strong acid. The iodometric estimation gives the evidence of one mole of peroxide to be bound per mole of the -μ-peroxo complex The LMCT bands of the peroxo group[35] are observed at 331 and 345 nm The dioxygen complexes are reversible with respect to oxygen uptake. The structure of the complexes is shown in Fig 4

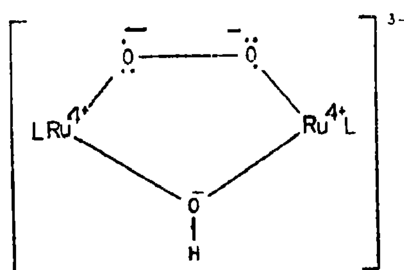


Fig 4

The Ru(III) EDTA or HEDTA-dioxygen complexes are the first examples of the -μ-peroxo complexes of a 4d transition element in aqueous solution and in the solid state. The Co(III)-μ-peroxo complexes as mentioned in the beginning of this article are known from the time of Werner.

The dioxygen complexes of heavier transition metal ions hold lot of promise in future as catalysts in various oxidation and atom transfer reactions of molecular oxygen[1]. One of their possible applications is in the design of fuel cells where oxygen can be reduced to water at a potential of 1.23 volts.

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NMR Spectroscopy of Oriented Molecules and its Applications to Inorganic Chemistry

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Principles and spectral details of nmr spectroscopy of oriented molecules are discussed. Differences in the appearance and the information-content between the spectra in isotropic and anisotropic media are described. Applications and limitations of the technique to inorganic chemistry are critically examined. A review of the work done in the area of structural studies of inorganic and organometallic compounds is presented.

THE technique of nmr spectroscopy of molecules oriented in anisotropic solvents such as those of nematic phases of liquid crystals[1] has been extensively applied to structural and conformational studies and the derived information has been summarised from time to time[2-11]. A survey of the literature reveals that the application of the technique to inorganic and organometallic chemistry is relatively scarce probably due to relatively poor solubilities and the complexities of such systems in general. On the other hand, it is also evident from the available literature that the technique provides unique structural, conformational and spectral information. The availability of highly sensitive and sophisticated FT-NMR equipments with multinuclear capabilities ensures bright prospects of research in this area. It is, therefore, pertinent to summarise potential applications of the technique with particular reference to inorganic chemistry.

Principles and Experimentation

The theory of nmr spectra of oriented molecules is well known. It is similar to that of the spectra in isotropic media except that the spin Hamiltonian describing such spectra contains additional terms due to anisotropic interactions such as those involved in direct dipole-dipole couplings, chemical shift and indirect coupling anisotropies and quadrupole coupling constants. Consequently, the spectra provide additional information carried by the anisotropic interactions. For spin 1/2 nuclei, the line positions and the line intensities of the spectra in diamagnetic materials are, therefore, influenced by the chemical shift ($\nu_i - \nu_j$) including the contribution due to chemical shift anisotropy, indirect spin-spin couplings (J_{ij}), direct dipolar couplings (D_{ij}) and anisotropic contributions of indirect couplings (D_{ij}^{ind}) where i and j are the two interacting nuclei. For H-H couplings, usually D_{ij}^{ind} is negligible and hence in such cases the obtainable additional information is that contained by the chemical shift anisotropy and the direct dipolar couplings. Since the direct dipolar couplings are inversely proportional to the cubes of the distances between the interacting nuclei, their determination provides a precise method for the determination of molecular shapes - an information which cannot be obtained in the liquid phase directly by any other technique. The most convenient anisotropic medium is provided by the nematic phase of liquid crystals. If a molecule is dissolved in such a medium, it experiences orientational effects unlike in an isotropic medium where all orientations of the dissolved molecules are equally probable. The orientation of the molecules dissolved in liquid crystals is described by the order matrix {S}, the elements (S_{ij}) of which are given by equation (1):

$$S_{ij} = \tfrac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle \quad \tfrac{1}{2}(3\cos^2\alpha - 1) \quad \ldots \quad (1)$$

where θ_{ij} is the angle which the axis joining nuclei i and j makes with the liquid crystal optic axis and α is the angle between the direction of the magnetic field and the liquid crystal optic axis. For liquid crystals, $\alpha = 0°$ or $90°$ depending upon the sign of the diamagnetic anisotropy of the liquid crystal and hence, the factor $\tfrac{1}{2}(3\cos^2\alpha - 1)$ in equation (1) is either 1 or $-\tfrac{1}{2}$.

If the axis connecting the nuclei i and j makes angles of θ_x, θ_y and θ_z with the axes x, y and z of the molecule-fixed Cartesian coordinate system, S_{ij} is written as

$$S_{ij} = \sum_{p,q} \cos\alpha_p \cdot \cos\alpha_q \cdot S_{pq} \quad \ldots \quad (2)$$

where p,q refer to the x,y,z axes of the coordinate system. The relationship between the degrees of order of various axes is implicit in equation (2).

The average molecular order is defined by a symmetric and traceless tensor with five independent elements. An appropriate selection of the molecule-fixed coordinate system reduces the number from 5 (for a system without a plane of symmetry) to 0 (for a case with cubic or spherical symmetry). If the molecule has a 3-fold or higher axis of symmetry, its selection as one of the axes leaves only one independent parameter. When there are two

perpendicular planes of symmetry each containing two axes of the Cartesian coordinate system, two independent values specify the molecular order. If the molecule possesses a single plane of symmetry containing two of the axes of the Cartesian coordinate system, 3-independent S-values define the molecular order.

The relation between the dipolar coupling (D_{ij}) and the order parameter is given by (3):

$$D_{ij} = -\frac{h\gamma_i\gamma_j}{4\pi^2} \cdot \frac{S_{ij}}{r_{ij}^3} \quad .. \quad (3)$$

where γ is the magnetogyric ratio and r_{ij} is the distance between nuclei i and j.

Relations between other anisotropic parameters and order parameters can be found in the literature in general. The chemical shift anisotropy ($\Delta\sigma_i$) of a nucleus in a 3-fold symmetry is given by (4):

$$\Delta\sigma_i = \frac{3}{2} \cdot \frac{\sigma_{ia}}{S_{zz}} \quad .. \quad (4)$$

where σ_{ia} is the chemical shift in the anisotropic medium with respect to that in the isotropic phase and S_{zz} is the order parameter of the symmetry axis

The methods of analysing the spectra in the anisotropic media are in general similar to those in the isotropic media. In fact, the Hamiltonian for an isotropic system transforms to that in an anisotropic medium if in the diagonal and the off-diagonal contributions to all the elements of the matrix, J_{ij} is replaced by ($J_{ij}+2D_{ij}$) and ($J_{ij}-D_{ij}$) respectively and in the chemical shift term, ($1-\sigma_i$) is substituted for ($1-\sigma_i-\sigma_{ia}$) where σ_i and J_{ij} are the chemical shift and the indirect spin-spin couplings observed in the normal high resolution spectra in the isotropic media.

The proton spectra of molecules oriented in thermotropic liquid crystals are in general strongly coupled unless heteronuclei are involved in the interactions Therefore, they are generally not amenable to first order analysis unlike most of the spectra in the isotropic media Computer programmes are now available for the iterative analysis of the spectra. The programmes which are most commonly used to provide the best-fit spectral parameters, namely, the chemical shift, the direct and the indirect spin-spin couplings are referred as LAOCOONOR[12] and LEQUOR[13] A typical spectrum is shown in Fig. 1

Once the direct dipolar couplings are derived from the analysis of the spectra of oriented molecules, the next step is to interpret them in terms of molecular geometry and the order parameters. If the number of independent dipolar

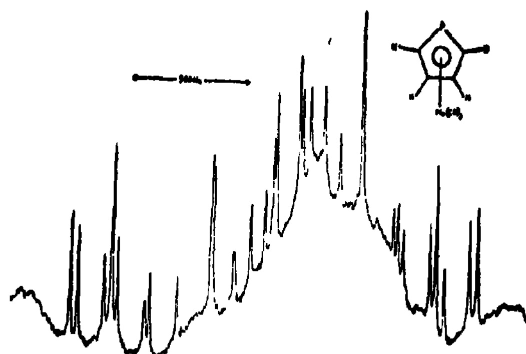


Fig. 1. Proton magnetic resonance spectra of phospha cymantrene (π-phospholyl manganese tricarbonyl) oriented in the nematic phase of Merck Phase IV Solute concentration 3 mole per cent, temperature 27°, spectrometer frequency 90 MHz

couplings equals the sum of the geometrical and the order parameters to be derived, one can solve simultaneous equations connecting the various parameters If, however, the number of the independent dipolar couplings is less than the 'sum' as defined above, one cannot derive the complete geometry-information unless one makes certain assumptions on the molecular geometry; the minimum number of such assumptions equals the number by which the direct couplings fall short of the 'sum' If the number exceeds the 'sum', an iterative procedure which computes the molecular geometry and the order by a weighted least-square-fit procedure is used The computer program SHAPE[14] is most commonly used for such a purpose.

Equation (3) connecting the dipolar couplings and the order parameters shows that if S_{ij} and r_{ij}^3 are changed by a constant factor, D_{ij} and hence the spectrum remains unchanged Since S_{ij} has also to be determined from the nmr experiment and it needs the knowledge of an internuclear distance, nmr studies of oriented molecules provide molecular shapes, i e, relative internuclear distances and the bond angles

An illustrative example of the procedure for the determination of molecular geometry of phosphine is discussed in detail before a general review of the applications to inorganic chemistry is presented Typical proton magnetic resonance spectrum of phosphine (PH_3) oriented in a nematic solvent is shown in Fig 2 The spectrum consists of doublets of a triplet The triplet with the intensity ratio of 1 : 2 : 1 arises from the HH dipolar coupling (D_{HH}) The spacing between the extreme lines corresponds to 6 D_{HH} Each component of the triplet is further split into 1 : 1 intensity doublets due PH indirect and direct spin-spin couplings (J_{PH} and D_{PH} respectively) with spacings equal to ($J_{PH}+2D_{PH}$). If J_{PH} is determined from the spectrum in the isotropic medium, the proton spectrum of phosphine provides D_{PH} and D_{HH} The relation (5) between

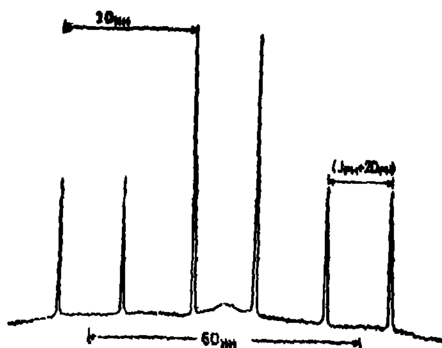


Fig 2 A typical proton magnetic resonance spectrum of phosphine oriented in a nematic solvent

the dipolar couplings and the HPH bond angle (α) can then be used to determine the bond angle

$$\frac{D_{PH}}{D_{HH}}=16\left(\frac{\gamma_P}{\gamma_H}\right)\sin^3 \alpha/2\,(2\sin^2 \alpha/2-1) \quad \ldots \quad (5)$$

Applications in Inorganic Chemistry

The applications in this direction have mainly been in the area of organometallic chemistry. The structure, conformation and chemical shift anisotropy have been investigated in a variety of organometallic compounds containing Cr, Mn, Fe, Ni, Ge, As, Se, Ru, Re, Cd, Sn, Sb, Te, W, Os, Pt and Hg as the metals A large number of inorganic and organophosphorus compounds have also been examined The bromine-pyridine charge transfer complex has also been studied[15].

The available literature can be summarised under the following heads : the investigations on (1) π-complexes, (2) other metallic compounds, (3) phosphorus compounds and (4) weak molecular complexes

(1) *π-Complexes* : The first inorganic complex to be studied was π-cyclobutadiene iron tricarbonyl[16]. The ring skeleton of the molecule is planar and the iron tricarbonyl moiety is involved in the formation of the π-complex with the π-electrons of the ring The proton spectrum of the molecule can be analysed analytically, using the expressions reported in the literature or iteratively using the computer programme. An interpretation of the dipolar couplings indicates significant deviations from the square geometry of the ring skeleton. Therefore, the ring has a symmetry less than D_{4h} although the permutation group symmetry of the nuclear spins has a 4-fold axis. It may, probably, be due to the fact that the molecule interconverts rapidly between non-square equilibrium conformers. The angle between the symmetry and the Fe-C axes is estimated as 61 ± 3°. In this case, it was not possible to determine the sign of the order parameter since the relative signs of the direct and the indirect couplings could not be determined. In π-benzene chromium tricarbonyl, it was clearly established[17] that in the thermotropic solvent formed by the mixture of N-(p-methoxybenzylidene)-p-amino-α-methyl cinnamic acid-n-propyl ester and p-(p-methoxyphenylazo)-phenyl-n-hexanoate, the molecule orients preferentially with the plane of the benzene ring along the direction perpendicular to the plane of the ring Significant deviations from the regular hexagonal geometry of the benzene ring have been studied in π-benzene chromium tricarbonyl.

The 5-membered ring system, namely, π-cyclopentadienyl manganese tricarbonyl[18-21] and its methyl derivative[22] have also been investigated In the case of cyclopentadienyl manganese tricarbonyl also, significant deviations from the regular pentagonal geometry of the ring system have been observed. The C-C bond distance between the carbonyl carbons in π-cyclopentadienyl iron tricarbonyl has been obtained as 2 78 Å In π-methylcyclopentadienyl manganese tricarbonyl, the ring protons do not deviate significantly from the regular pentagonal arrangement. In addition, the rotation of the methyl group about the C-C bond is found to be hindered in a 3-fold potential due to the presence of the $Mn(CO)_3$ group.

In π-cyclopentadienyl nickel nitrosyl[23] and tricarbonyl tungsten hydride[24,25], the ring skeletons have been found to be regular pentagonal.

In *bis*(cyclopentadienyl) mercury[23], the spectrum is consistent with the σ-bonded structure if, and only if, there is some kind of averaging. The spectrum corresponds to symmetry achieved either by an exchange process or a bond-shift mechanism. The ratios of the interproton distances correspond to those expected for a regular pentagon.

The structure of the 1,3-butadiene moiety of 1,3-butadiene iron tricarbonyl which has been a puzzle for the past several years has been established to be non-planar[26] The distances between the *anti* protons from the remaining four protons is determined as 0 77 ± 0 06 Å In π-allyl tetra carbonyl rhenium, the π-allyl group has been found to be non-planar[27].

A new application of nmr spectroscopy of oriented molecules has been discovered from the studies on phosphacymantrene and comparison of the results with geometrical data obtained for several 5 and 6 membered heteroaromatic molecules[28-30]. The results have led to the discovery of a new method for the determination of covalent and van der Waals radii. It is found that in such system, certain interproton distance ratios are related inversely to the covalent and the van der Waals radii. The covalent radii of O, N(H), C(H), S, P, Se, Te and As have thus been determined. Their values agree well with those reported in the literature and determined by other techniques.

(2) *Other metallic compounds* : A large number of compounds such as silane[31], germane[31], tetramethyltin[32], methyl mercury halides[33,34] and

itrate[35], methyl tin chloride[36], methyl trichlorosilane and stannane[37], methyl germane[38], dimethylmercury[38], cadmium[39], selenium[40] and tellurium[40], 1,1,1-trifluoromethyl methyl mercury[41], 2, 1, 3-benzoselenadiazole[42], benzoselenyl chloride[43], selenophene[44], benzoselenophene[45], 2,2′-biselenophene[46], selenophene-2-carbaldehyde[47] *bis* (ethane 1,2-dithiolato) nickel(IV)[48,49], trimethylene-methane-iron tricarbonyl, trihydro nona carbonyl methyl carbene tri osmium (or ruthenium)[47,50,51] and ac-dichloro-b-ethylene pyridine (-d_5) platinum(II)[52] have been studied.

Possible mechanism of distortions from tetrahedral symmetry in silane, germane and tetramethyl tin have been studied. In methyl mercury halides, the proton spectra including ^{13}C and ^{199}Hg have been investigated. The HCH bond angles of 110 00±0.04°, 110.10 ± 0 03° and 110 20 ±0.03° have been determined for the chloro, the bromo and the iodo compounds respectively. The corresponding HHgC angles are 23.74°, 23.75° and 23.76°. A rapid halogen exchange has been observed in these compounds. The proton chemical shift anisotropy is 2 4, 2 6 and 2 8 ppm respectively for methyl mercury chloride, bromide and iodide. The mercury shielding anisotropy value of 5345 ppm has been obtained for methyl mercury bromide. In methyl mercury nitrate, the molecular geometries in the lyotropic and the thermotropic solvents are similar, indicating negligible solvent-solute interactions. The Sn-C-H bond angle of 107.4° has been obtained in methyl tin chloride. From the ^1H, ^{13}C, ^{29}Si, ^{117}Sn and ^{119}Sn spectra where M-C dipolar couplings were also observed, the molecular structures of methyl trichlorosilane and stannane have been determined.

In methyl germane, the relative conformations of the CH_3 and GeH_3 fragments are staggered or rotate freely about the Ge-C bond and the HCH bond angle is 108°48′. Values of the HHgC angle and HCH bond angles in dimethyl mercury have been determined as 23.10° and 108.36° respectively. The angle between the H-Cd bond and the C_3-axis of symmetry and the HCH bond angle in dimethyl cadmium are determined as 23.04±0.13° and 108 12° respectively. In contrast to dimethyl mercury and cadmium which have 3-fold axes of symmetry, dimethyl selenium and tellurium have only 2-fold symmetry axes. The proton spectra including the ^{13}C and the ^{77}Se (or $^{123/125}Te$) satellites have been studied and the HCH bond angles in dimethyl selenium and tellurium have been determined as 110 142° and 110.799° respectively. The corresponding H-C-metal angles are 106.22° and 107.34°. In 1,1,1-trifluoro-methyl methyl mercury, precise determination of molecular geometry was difficult due to low degree of molecular order in the various solvents used and due to solvent and temperature dependence of the indirect spin-spin couplings.

The structures of 2,1,3-benzoselenadiazole, benzoselenyl chloride and benzoselenophene have been determined. Considerable bond fixation in the 6-membered ring has been observed in 2,1,3-benzoselenadiazole. In benzoselenyl chloride, the phenyl ring geometry does not deviate significantly from the regular hexagonal arrangement of the protons. The Se-C bond length is estimated as 1.97 Å. The proton spectrum of 2,2′-biselenophene including ^{77}Se-H satellites shows that the molecule exists as an equilibrium between two twisted conformers with the transoid one being more abundant; the angle of twist is 25±5°. In selenophen-2-carbaldehyde, the dominant existence of the Se-O *cis*-conformer is indicated.

Bis (ethane-1,2-dithiolato)nickel has been studied at various temperatures. The results are consistent with the fact that the two organic ligands rotate with respect to each other. The HH distance ratios in trismethylene methane iron tricarbonyl have been determined. The M-H-M bond angles in trihydrononacarbonyl methyl carbene tri osmium (or ruthenium) have been estimated as 103° and 101° for the osmium and the ruthenium compounds respectively. The relative proton and platinum positions have been determined in ac-dichloro-b-ethylene pyridine (d_5) platinum(II) complex. It is found that the equilibrium structures have the pyridine ring inclined at an angle to the $PtCl_2$ plane with rapid reorientation between the symmetry related forms.

(3) *Phosphorus compounds*: A number of phosphorus compounds[53] such as phosphine[54], phosphorus trifluoride[55], phosphoryl fluoride[56], hexafluoro cyclophosphazene[57], hexachloro cyclophosphazene[57], octachloro cyclophosphazene[57], phosphorus sesquisulphide[58], phenylphosphine[59], cyclotetra phosphines[60], ^{13}C-triply labelled tribenzoyl phosphine[61], trimethyl phosphine selenide[62], difluorophosphine selenide[63], phenyl ester of dichloro phosphoric acid[64], methyl phosphonate[65], isotopically labelled (with ^{13}C and ^{15}N) *bis*(dichlorophosphino) methylamine[66], trimethyl-phosphine, phosphine oxide, sulphide and selenide[67-69], cyclotetra phosphanes[70] and hexaphenyl cyclohexaphosphine[71] have been investigated.

The HPH bond angle in phosphine has been determined as 94 73 ± 0 05° and the ^1H and the ^{31}P chemical shift anisotropies are -7 5 and 955.5 ppm respectively. In phosphorus trifluoride the FPF bond angle is 97 8° and the ^{19}F and ^{31}P chemical shift anisotropies are -49 ± 5 and 228 ± 2 ppm respectively. From studies of the ^{19}F and the ^{31}P nmr spectra at various temperatures in phosphonyl fluoride, the FPF bond angle and the ^{19}F and the ^{31}P-chemical shift anisotropies have been determined. The spectrum of octachlorocyclophosphazene corresponds to the D_{4h}-symmetry of the molecule. The ring-folding in cyclo-tetraphosphines has been estimated. The CPH bond angle in phenyl phosphine is determined as 96.4 ± 1.0°. The chemical shift anisotropy in hexafluoro (and chloro) cyclophosphazene and phosphorus sesquisulphide have been determined.

From the proton decoupled ^{13}C and ^{31}P nmr spectra of ^{31}C-triply labelled tribenzoyl phosphine, the CPC bond angle and the ^{31}P-chemical shift anisotropy are determined as 95 9 ± 0.2° and 75 ± 15 ppm respectively. In the phenyl ester of dichlorophosphoric acid, the dihedral angle between the C-O-P and the phenyl planes is determined as 49° from the ^{1}H and the ^{31}P nmr spectra. The HCH bond angle in methyl phosphonate is determined as 109 6°. Nuclear magnetic double resonance studies of isotopically labelled (with ^{13}C and ^{15}N) *bis*(dichlorophosphino) methyl amine provide the P-N-P angle as 117 0 ± 0 5° and the distance ratio r_{PN}/r_{OH} as 1.527

The ^{13}C-chemical shift anisotropies in the $(CH_3)_3X$ compounds are 0 + 5, 34 + 10, 8 ± 10 and 18 + 10 ppm for X=P, PO, PS and PSe respectively and the corresponding C-P-C bond angles are 99 2, 105 7, 104 7 and 105 0°. The ring conformation of hexaphenyl cyclohexaphosphine determined from the nmr studies in the liquid phase agrees well with the X-ray data in the solid state The 6-membered ring puckering angle is estimated to lie between 96 5-97°

(4) *Weak molecular complexes* : The technique has also been applied to study charge transfer, hydrogen bonded and other weak molecular complexes. The charge transfer complex between pyridine and bromine is found to be linear such that the two bromines are on the C_2-axis of symmetry[15]. The interproton distance ratios in the complex have been determined. The values are significantly different from those in pyridine A trimethyltin-pyridine (d_5) complex has also been investigated[26,72]. The configurational changes around the tin atoms have been observed as a result of the complex formation The C-Sn-C bond angle in trimethyltin changes from 113 9° without pyridine to a value of 120° in presence of pyridine. The results are in agreement with 1 1 complex formation between trimethyltin chloride and pyridine. Dipolar couplings between the protons of trimethyltin chloride and the deuterons of pyridine were not observed implying a fast exchange between the bound and the free states.

Conclusion

It is seen that the technique of nmr spectroscopy of oriented molecules can be applied to a variety of structural and conformational problems in inorganic chemistry. The studies on the weak molecular complexes provide unique information in the liquid phase.

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Dithiophosphinates of Some First Row Transition Metals

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The effect of substitution on the phosphorus atom of dithiophosphinates was examined by synthesising complexes of Etdtpi, Cl_2dtpi and MeCldtpi [where Etdtpi, Cl_2dtpi and MeCldtpi are di (*p*-ethylphenyl), di (3,4-dichlorophenyl) and di(2-methyl-5-chlorophenyl)dithiophosphinate] with Cr(III), Mn(II), Fe(III), Co(II) and Ni(II). The esr spectra of Fe(III) derivatives were indicative of distortion from octahedral symmetry while for those of Cr(III) derivatives a large reduction of the spin-orbit coupling constant (λ) was observed, indicating the high nephelauxetic effect of these sulphur ligands. Wherever possible the ligand field parameters (10 Dq, B and β) were evaluated and from the 10 Dq values the position of these sulphur ligands were found to be lower in the spectrochemical series compared to many other dithioligands.

THE effect of substituents on the spectral properties of dithiocarbamato complexes has been observed[1] In an earlier communication the stability of cupric dithiophosphinates in relation to the substituents on the phosphorus atom was reported[2]. In view of this it was of interest to investigate the dithio derivatives of some other first row transition metals with various substituted dithiophosphinic acids. The results of such a study on the complexes of Etdtpi, Cl_2dtpi and MeCldtpi are reported here.

Experimental

The magnetic moment measurements were carried out at room temperature on a Gouy balance using Hg[Co $(SCN)_4$] as the calibrant. The electronic and esr spectra were recorded on Perkin-Elmer 402 spectrophotometer and E-line Century Series Varian X-band spectrometer respectively.

Preparation of the complexes:

CrX_3 (X=Etdtpi, Cl_2dtpi or MeCldtpi): Methanolic solutions of the sulphur ligands (3 0 g) and chromium chloride hexahydrate (0 7 g) were mixed and refluxed for about 20 min The bluish violet or violet complexes which separated out were filtered, washed with methanol and recrystallised from chloroform-methanol mixture.

MnX_2(X=Etdtpi, Cl_2dtpi or MeCldtpi): Methanolic solutions of the sulphur ligands (3.0 g) and $MnCl_2.6H_2O$ (0 9 g) were mixed with vigorous stirring. The yellow complexes were washed with methanol and dried under vacuum.

FeX_3 (X–Etdtpi, Cl_2dtpi or MeCldtpi) : Excess amount of the methanolic solution of the sodium salt of the sulphur ligands were added to a ferric chloride solution in methanol with vigorous stirring. The black/olive green complexes were filtered, washed with methanol and dried.

Co(Cl_2dtpi)$_2$: The complex was precipitated when an aqueous solution of cobalt chloride hexahydrate (1.4 g) was mixed with NaCl_2dtpi (3.8 g) in water. The dark green complex was filtered and dried. The attempted preparation in methanol resulted in a brown sticky mass of uncertain composition. Co(Etdtpi)$_2$ was prepared in solution by mixing appropriate amount of the methanolic soluions of $CoCl_2.6H_2O$ and EtdtpiH.

Ni (MeCldtpi)$_2$: A methanolic solution of nickel chloride hexahydrate (1.5 g) was added to a methanolic solution of NaMeCldtpi and the precipitated light violet complex was filtered, washed with methanol and dried.

TABLE 1—COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	Found (%)				Calcd. (%)			
		M	S	C	H	M	S	C	H
Cr(Etdtpi)$_3$	Violet	5.52	20.41	57.60	5.32	5.37	19.87	59.57	5.58
Cr(Cl_2dtpi)$_3$	Bluish violet	4.18	15.61	45.95	1.59	4.29	15.83	35.61	1.48
Cr(MeCldtpi)$_3$	Violet	4.68	17.49	46.45	3.10	4.77	17.61	46.24	3.30
Mn(Etdtpi)$_2$	Yellow	8.13	19.38	57.92	5.12	8.27	19.25	57.74	5.41
Mn(Cl_2dtpi)$_2$	Yellow	6.28	15.64	34.50	1.21	6.65	15.48	34.82	1.45
Mn(MeCldtpi)$_2$	Brown	7.58	17.62	45.21	3.62	7.36	17.14	44.98	3.21
Fe(Etdtpi)$_3$	Black	5.83	19.53	59.81	5.35	5.76	19.78	59.33	5.56
Fe(Cl_2dtpi)$_3$	Olive green	4.69	15.65	35.86	1.27	4.60	15.82	35.59	1.48
Fe(MeCldtpi)$_3$	Olive green	5.32	17.86	46.18	3.08	5.11	17.55	46.07	3.29
Co(Cl_2dtpi)$_2$	Dark green	6.92	15.49	45.20	2.94	7.08	15.37	44.80	3.20
Ni(MeCldtpi)$_2$	Light violet	7.82	17.18	33.80	1.52	7.68	17.05	34.60	1.44

TABLE 2—MAGNETIC MOMENTS AND THE SOLUTION SPECTRAL DATA* OF THE COMPLEXES

Complex	Magnetic moment (B.M.)	Band maxima (cm^{-1})
$Cr(Etdtpi)_3$	3.83	13620, 17860, 18950(sh)
$Cr(Cl_2dtpi)_3$	3.90	13890, 18180, 19230(sh)
$Cr(MeCldtpi)_3$	3.86	13900, 18180, 19220(sh)
$Mn(Etdtpi)_2$	5.81	21100
$Mn(Cl_2dtpi)_2$	5.85	17540(sh), 21200
$Mn(MeCldtpi)_2$	5.80	21700
$Fe(Etdtpi)_3$	–	16600, 19000, 23500
$Fe(Cl_2dtpi)_3$	5.57	16260, 19050, 23800
$Fe(MeCldtpi)_3$	5.80	14900(sh), 17540(sh), 22730
$Co(Etdtpi)_2$	–	14900
$Co(Cl_2dtpi)_2$	4.45	15000
$Ni(Etdtpi)_2$	–	13700, 17900
$Ni(MeCldtpi)_2$	–	13890, 18180

*All the spectra were recorded in chloroform.

The analytical data of the complexes are given in Table 1 and magnetic moment and solution spectra in Table 2.

Results and Discussion

Cr(III) complexes : The complexes were soluble in organic solvents and had room temperature magnetic moments in the range 3.83-3.90 B.M. obtained by the Gouy's method. This was in good agreement with those obtained by Evans' nmr technique[8] (3.77-3.81 B.M.). The electronic spectra were typical of octahedral CrS_6 core complex showing intense absorptions around 13620-13900 cm^{-1} and 17860-18180 cm^{-1} corresponding to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) transitions respectively. The shoulders observed around 18950-19230 cm^{-1} may originate due to a trigonal split component of the ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition or can be due to a spin forbidden quartet-doublet transition[4].

The high value of the oscillator strength (Table 3) reflect the pronounced covalency in the metal-ligand bond. The 10 Dq values (13620-13900 cm^{-1}) were evaluated from the first spin allowed transition and using equation for B, the values of Racah parameter (399-402 cm^{-1}) were obtained. A comparison of the 10 Dq and B values (Table 3) suggest that the substitution in the benzene nucleus attached to the phosphorus atom does not significantly influence the ligand field parameters.

with a peak to peak separation of 300 G were obtained. The $g_{isotropic}$ values were calculated to be 1.98±0.01. The large reduction of the spin-orbit coupling constant (28-38 cm^{-1}) compared to the free ion value (90 cm^{-1}) is a measure of metal-ligand covalency and was in good agreement with the high nephelauxetic effect of these sulphur ligands.

Mn(II) complexes : Among the manganese(II) dithio derivatives $Mn(Etdtpi)_2$ was found to be unstable. $Mn(Cl_2dtpi)_2$ and $Mn(MeCldtpi)_2$ had low solubility in non-polar solvents with room temperature magnetic moments in the range of 5.80-5.85 B.M. and the electronic spectra in chloroform showed a band around 21000 cm^{-1} which could be due to a d-d transition. The esr spectra of the powder samples showed only a single line. However, when diluted with analogous zinc matrix, six hyperfine lines ($I = 5/2$) were observed with g and A values in the ranges 2.02-2.03 and 80-95 (Gauss) respectively.

Fe(III) complexes : The black $Fe(Etdtpi)_3$ was found to be unstable whereas $Fe(Cl_2dtpi)_3$ and $Fe(MeCldtpi)_3$ were stable but decomposed on prolonged exposure to air, similar to other ferric dithio complexes. The room temperature magnetic moments were in the range of 5.57-5.80 B.M. and bands around 16000, 19000 and 23500 cm^{-1} were observed in the electronic spectra. The esr spectra of the powder samples both at room temperature as well as at 77°K showed three g-values (in the range of 7.38-7.67, 4.26-4.27 and 1.92-1.98) which reflect distortion from octahedral symmetry[5].

Co(II) complexes : Although dithiophosphinates, unlike other dithioligands, have been observed to form stable complexes of cobalt(II), it is of interest to note that in the present work only $Co(Cl_2dtpi)_2$ could be isolated in the solid state and $Co(Etdtpi)_2$ was studied in solution, the analogous derivative with MeCldtpi could not be formed

The magnetic moment of $Co(Cl_2dtpi)_2$ at room temperature was found to be 4.45 B.M., indicative of a tetrahedral geometry and the electronic spectrum in chloroform was typical of CoS_4 chromophore showing a multicomponent band

TABLE 3—LIGAND FIELD PARAMETERS OF Cr(III) and Co(II) COMPLEXES*

Complex	10 Dq(cm^{-1})	B(cm^{-1})	β	Oscillator strength	λ (cm^{-1})
$Cr(Etdtpi)_3$	13620	399	0.43	365 (13620), 367 (17860)	28
$Cr(Cl_2dtpi)_3$	13890	402	0.43	379 (13890), 370 (18180)	38
$Cr(MeCldtpi)_3$	13900	401	0.43	419 (13900), 365 (18180)	38
$Co(Etdtpi)_2$	3950	763	0.67	–	–
$Co(Cl_2dtpi)_2$	3702	793	0.70	–	−124

* Oscillator strengths were calculated from the relation $f = 4.6 \times 10^{-9} \epsilon_{max} \nu_{1/2}$, ϵ_{max} = molar extinction coefficient $\nu_{1/2}$ = band width at the half height in wave numbers. The bands oscillator strengths are given in parenthesis.

The esr spectra of the powder samples were recorded at room temperature and broad signals

centered around 15000 cm^{-1} which was assigned to ${}^4A_2 \rightarrow {}^4T_1(P)$ transition[6]. Using equations given

elsewhere[7] the 10 Dq and B values were calculated to be 3702 and 793 cm^{-1} respectively. Similar results were obtained for $Co(Etdtpi)_2$ as given in Table 3. The value of the nephelauxetic parameter β was evaluated to be 0 70 and 0 67 for $Co(Cl_2dtpi)_2$ and $Co(Etdtpi)_2$ respectively. Using[7] the magnetic data and Dq values λ was obtained as -124 cm^{-1} for $Co(Cl_2dtpi)_2$ and the reduction in its magnitude from the free-ion value (-178 cm^{-1}) indicated a substantial metal-ligand covalency.

Ni(II) complexes : $Ni(MeCldtpi)_2$ was isolated in the solid state while $Ni(Etdtpi)_2$ could be studied in solution and with Cl_2dtpi no complex was formed The solution spectra of $Ni(MeCldtpi)_2$ and $Ni(Etdtpi)_2$ in chloroform showed bands around 13890, 18180 cm^{-1} and 13700 and 17900 cm^{-1} respectively which are diagnostic[8] of a diamagnetic square planar structure. The lowest transitions at 13700 and 13890 cm^{-1} were assigned to $d_{x^2-y^2} \rightarrow d_{xy}$ transition in a D_{2h} symmetry. The 10 Dq values (16500 and 16690 cm^{-1}) were calculated by using relations given elsewhere[9] and are in agreement with the position of dithiophosphinates in the spectrochemical series[10].

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Photochemical Reduction of Uranyl Ion with Tri-*p*-Tolylphosphine

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Photochemical reduction of uranyl ion with tri-*p*-tolylphosphine is temperature independent and obeys second order kinetics. Higher value of chemical quenching constant kq, 165.0 LM^{-1} for tri-*p*-tolylphosphine as compared to that for triphenylphosphine 147.0 LM^{-1} suggests participation of inductive effect of methyl group at *p*-position. A dynamic mechanismfor oxygen atom transfer from excited uranyl ion to ground state of tri-*p*-tolylphosphine has been suggested.

THE photochemistry of uranyl ion has been studied employing flash photolysis and esr techniques. It has been shown that organic compounds reduce uranyl ion via inter or intra electron transfer or via hydrogen atom abstraction from the carbon atom adjacent to an activating group such as -CO-,-CN, -COOH, -CHO,-OH, $-CONH_2$ or -COOR[1,2]. In earlier investigations on photochemical reduction of uranyl ion with triphenylphosphine, triphenylarsine, triphenylantimony and triphenylbismuth, oxygen atom transfer from uranyl ion to the substrates has been suggested[3] In the present investigation, kinetics and mechanism for photochemical reduction of uranyl ion with tri-*p*-tolylphosphine have been investigated.

Methods and Material :

Uranyl acetate (B D H., England) and sulphuric acid (B D H.) AnalaR grade were used as such and tri-*p*-tolylphosphine was prepared and purified as reported in the literature[4] Double distilled deionized water-acetone (AnalaR grade) (3 7 v/v) were used as the reaction medium. Photochemical reduction was investigated in pyrex glass photochemical reactor Temperature of the reaction mixture was controlled by circulating water with MK-70 cryostat Oxygen free nitrogen gas was flushed through the reaction mixture and its progress was followed by observing the concentration of uranium(IV) formation with VSU 2-P spectrophotometer. Quantum yield for uranium(IV) formation was determined using potassium ferrioxalate as an actinometer[5].

Results and Discussion

Photochemical reduction of uranyl ion with tri-*p*-tolylphosphine follows pseudo first order kinetics with respect to each of the uranyl ion and tri-*p*-tolylphosphine and overall reaction was of second order. Rate and quantum yield for uranium(IV) formation are linear functions of tri-*p*-tolylphosphine concentration (Table 1).

Tertiary phosphines have electronic absorption spectra in the region 250-300 nm (due to $n \rightarrow \pi^*$ transition). Pyrex glass photochemical reactor cut off electromagnetic radiations <365 nm

TABLE 1—QUANTUM YIELD (ϕ) FOR URANIUM(IV) FORMATION AND SECOND ORDER RATE CONSTANTS [K] I_0 = 3 02 × 10^{16} q/s AND T = 30°

$[UO_2^{2+}]$ M L^{-1}	[t-*p*-TP] M L^{-1}	$[H^+]$ M L^{-1}	ϕ	K min^{-1}
0 005	0 010	0 40	0 22	0 250
0 010	0 010	0 40	0.22	0 161
0 015	0 010	0 40	0 20	0 108
0 020	0 010	0 40	0 23	0 075
0 025	0 010	0 40	0 24	0 090
0 010	0 0050	0.40	0 17	0 260
0 010	0 0075	0 40	0 19	0 184
0 010	0.0100	0 40	0 22	0 161
0 010	0 0150	0 40	0 27	0 132
0 010	0 010	0,10	0 09	0 066
0 010	0 010	0 20	0 15	0 108
0 010	0.010	0 40	0 22	0 161
0 010	0.010	0 80	0 27	0 200

Protonation of uranyl ion with sulphuric acid shows a blue shift of 10 nm However, addition of tri-*p*-tolylphosphine does not show any change in the spectra, ruling out any ground state interaction between the reactants, indicating that uranyl ion is the only species which absorb the light radiations in the visible region. In the kinetic study of photoaccelerated uranium(IV)-uranium(VI) electron exchange reaction, it has been observed that radiations 540-550 nm and <600 nm, which are absorbed by uranium(IV) are inefficient for photoacceleration reaction. Hence uranyl ion is the only photoactive species[6].

During excitation of uranyl ion with lowest energy (singlet→triplet) transition, the electron moves from π-bonding highest occupied molecular orbital (HOMO) consisting of uranium 5f- and 6d-, and oxygen 2p-orbitals to lowest unoccupied molecular orbital (LUMO) mainly of uranium 5f-orbitals[7]. Consequently, increased electron density on the uranium atom reduces the net charge on it. Excitation of uranyl ion to higher singlet state may intercross to the lowest state which, because of its

sufficient energy and longer life time (spin forbidden nature of Triplet→Singlet), is the more reactive state. Oxidation potential of the uranyl ion in the excited state (2.6V) is higher as compared to that in the ground state (0.05V)[8]. Excitation of uranyl ion imparts to it some free radical character as a result of which U=O bond length is increased[7].

Product analysis of the photolysed solution shows a strong absorption band at 660 nm corresponding to uranium(IV) formation. Infrared absorption band at 1120 cm^{-1} of photolysed product (green crystals) shows co-ordinated phosphoryl group, whereas the infrared absorption band at 1190 cm^{-1} is due to tri-*p*-tolylphosphine oxide extracted with benzene from decomposed products in concentrated hydrochloric acid.

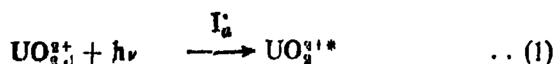
In the tri-*p*-tolylphosphine, phosphorus atom has low-lying vacant d-orbitals for π-bonding with oxygen 2p-orbitals[9]. The π-bonding ability of phosphorus atom facilitates transfer of oxygen atom from excited uranyl ion to tri-*p*-tolylphosphine. The inductive effect of methyl group at *para* position further increases the strength of σ-bond in addition to π-bonding of the phosphoryl group.

The temperature independent nature of the photochemical reduction of uranyl ion with tri-*p*-tolylphosphine eliminates collisional electronic energy transfer[1,10]. First excited state of tri-*p*-tolylphosphine is above the luminescent state (lowest triplet) of uranyl ion. Deactivation via collisional energy transfer from excited uranyl ion to ground state of tri-*p*-tolylphosphine is an endothermic process, not favoured energetically.

The photochemical reduction of uranyl ion may proceed by electron transfer via transient species, uranium(V), which in aqueous acidic solution immediately disproportionates to uranium(IV) and uranium(VI). Absence of electronic absorption band at 636 nm and 750 nm due to uranium(V) does not favour the electron transfer mechanism for photochemical reduction of uranyl ion with tri-*p*-tolylphosphine[11].

In view of above, a dynamic mechanism of oxygen atom transfer through exciplex formation has been suggested for photochemical reduction of uranyl ion with tri-*p*-tolylphosphine. Donor-acceptor interaction arises between the two in the excited state, although there is no affinity in the ground state.

The mechanism of the reactions is represented in Scheme 1.


$$UO_2^{2+} + h\nu \xrightarrow{I_a} UO_2^{2+*} \quad \dots (1)$$

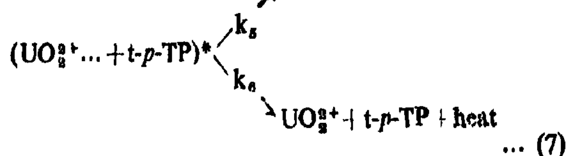

$$UO_2^{2+*} \xrightarrow{k_1} UO_2^{2+} + h\nu' \quad \dots (2)$$


$$UO_2^{2+*} \xrightarrow{k_2} UO_2^{2+} + \text{heat} \quad \dots (3)$$


$$UO_2^{2+} + UO_2^{2+*} \xrightarrow{k_3} 2UO_2^{2+} + \text{heat} \quad \dots (4)$$


$$UO_2^{2+*} + t\text{-}p\text{-TP} \xrightarrow{k_4} (UO_2^{2+} \dots + t\text{-}p\text{-TP})^* \quad \dots (5)$$


$$\xrightarrow{k_5} U(IV) + t\text{-}p\text{-TP=O} \quad \dots (6)$$


$$(UO_2^{2+} \dots + t\text{-}p\text{-TP})^* \xrightarrow{k_6} UO_2^{2+} + t\text{-}p\text{-TP} + \text{heat} \quad \dots (7)$$

Scheme 1

where t-*p*-TP is tri-*p*-tolylphosphine, k_1 is the fluorescence deactivation rate constant, k_2, k_3 and k_6 are radiationless deactivation rate contants, k_4 is the chemical quenching rate constant, which determine the rate of chemical quenching of excited uranyl ion by ground state of tri-*p*-tolylphophine and k_5 is the chemical decomposition deactivation of exciplex rate constant. Employing steady state principle for intermediates, a mathematical relation between the rate constants and quantum yield for uranium(IV) formation is derived :

$$\frac{1}{\phi} = \left[1 + \frac{k_6}{k_5}\right]\left[1 + \frac{k_1 + k_2 + k_3[UO_2^{2+}]}{k_4[t\text{-}p\text{-TP}]}\right] \quad \dots (8)$$

Plot between ϕ^{-1} versus reciprocal of tri-*p*-tolylphosphine concentration is a straight line (Fig 1) with an intercept $1 + \frac{k_6}{k_5} = 2.75$. Low values of quantum yield (ϕ) and $\frac{k_6}{k_5} = 1.75$ ($k_6 > k_5$) show that contribution of radiationless deactivation of excited uranyl ion is more as compared to the contribution made by chemical deactivation.

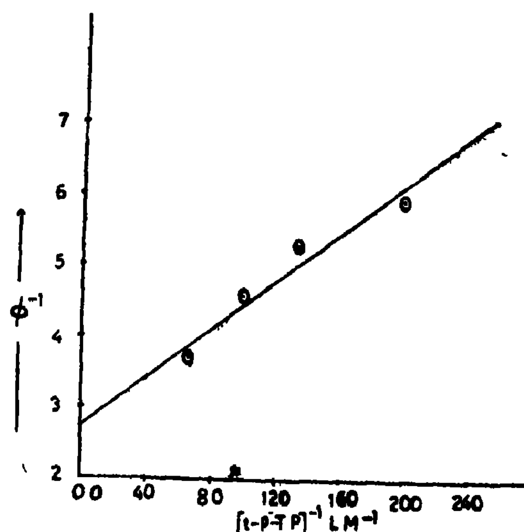


Fig 1

Ratio of the intercept to slope gives the magnitude of chemical quenching constant kq, which is a measure of radiationless chemical quenching of the opti-

cally excited uranyl ion.

$$\frac{\text{Intercept}}{\text{Slope}} = \frac{k_4}{k_1+k_2+k_3[UO_2^{2+}]} = kq \quad \dots (9)$$

or $kq = \tau_0 k_4$

where $\tau_0 = \frac{1}{k_1+k_2+k_3[UO_2^{2+}]}$

Higher value of $kq = 165.0\ LM^{-1}$ for tri-*p*-tolylphosphine as compared to that for triphenylphosphine[8] $147.0\ LM^{-1}$ is due to the inductive effect of methyl group present at the *para* position in phenyl group in triphenylphosphine.

Stern-volmer plot of $\frac{I_f^0}{I_f} = 1 + k_{sv}[Q]$ (Fig. 2.)

where I_f^0 and I_f are the fluorescence intensities in the absence and in the presence of quencher tri-*p*-tolylphosphine is a straight line with an intercept=1 and $K_{sv} = 222.2\ LM^{-1}$. Greater values of $K_{sv} = 222.2\ LM^{-1}$ as compared to $kq = 165.0\ LM^{-1}$ signify that physical quenching competes with the chemical quenching.

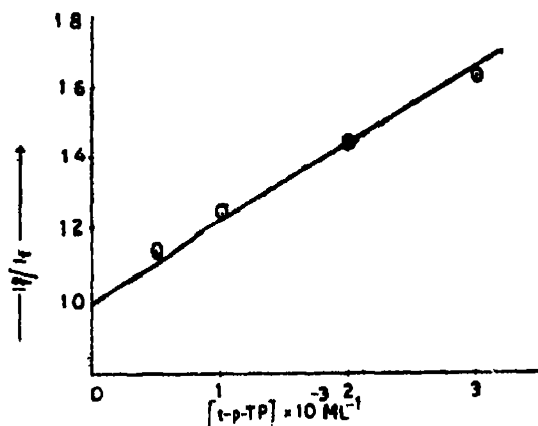


Fig 2

Aromatic molecules deactivate the excited uranyl ion through the π-complex formation between the aryl groups and the excited uranyl ion, since donor acceptor interaction can arise in the excited state[12]. Tri-*p*-tolylphosphine has three aryl groups with methyl group substituted at *p*-position (an electron releasing group) which further enhance the deactivation of excited uranyl ion. Solvent water deactivates the luminescent uranyl ion by hydrogen abstraction[13]. Co-ordinated water molecules deactivate via intramolecular energy transfer from uranyl ion to higher evertones of water molecules[1,14]. The physical quenching lowers the rate and quantum yield for uranium(IV) formation.

Quantum yield and rate of uranium(IV) formation are increased with an increase in hydrogen ion concentration. Protonation of uranyl ion establishes a fast equilibrium $UO_2^{2+} + H^+ \rightleftharpoons UO_2^{2+}H$ and have higher exidation potential and longer life time in the excited state[15,16].

Acknowledgement

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Complex Formation in Molten Salts : Thermodynamics of Association Equilibria of Single and Mixed Ligand Complexes : A Review†

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Study of association equilibria involving metal ion with single and mixed ligand in molten salts by EMF and computer methods is reviewed. Temperature coefficients of the association constants have been evaluated and applicability of quasi-lattice formulation examined.

THERMODYNAMICS of association equilibria in molten salts have been studied by several techniques as polarography chronopotentiometry, spectroscopy, solubility etc ; due to simplicity of technique, high degree of reproducibility and precision which can enable extrapolation and computer evaluation of data, EMF method has been widely used. The measurements in a molten salt electrochemical cell involve essentially the same considerations[1] as in an analogous aqueous cell, viz., the need for a reversible, responsive indicator and reference electrodes which would be stable at the temperature employed and in the corrosive environment imposed by the solvent and the need for boundary between solutions of different compositions. In this paper, studies on association equilibria involving single and mixed ligand complexes of metals as silver, thallium, cadmium, lead, cobalt *etc.* with halides, nitrite, cyanide, phosphate, sulphate, chromate, molybdate, iodate in single alkali and alkaline earth metal nitrates, sulphates and halides and their charge symmetric (solvents with equal number of cations and anions) and asymmetric (solvents with different number of cations and anions) mixtures are reviewed. The choice of the solvent systems is governed by considerations of melting point, thermal stability, ion-reactivity with electrodes and containers and non-hygroscopic and non-complexing nature of the components[2].

Molten Salt Electrochemical Cells

Studies have been carried out using the concentration cells with metal-metal ion (reversible to metal ion, cell A or through the solubility equilibrium of two metal oxides, cell C) and metal-insoluble metal halide (reversible to halide ion, cell B) as indicator electrodes The electrode reactions, equations for Nernst slope and activity coefficients are summarized in Table 1 Detailed description of cells, experimental technique, pretreatment of electrodes, solvent preparation *etc.* has been given[3-10]. The liquid junction potential has been considered to be negligible since the solutions are dilute and the same solvent is used on both sides of the junction.

Behaviour of reversible solid and liquid metal-metal ion as indicator electrode in halide and nitrate melts have been reported[11-17] One of the factors that favours the reversibility of the metal-metal ion electrode in molten salts is the increased rate of oxidation-reduction at the electrode surface giving rise to a large exchange current and a thermodynamically "well-behaved" electrode[12]. A disadvantage could arise[18-20] if the metal is easily oxidised Ag/Ag^+ electrode which has been extensively used as the indicator electrode, has been shown to be reversible[14], and since the oxides are easily volatilised from the surface below *c* 250°, the surface is free from oxide impurities

Ag-AgX(s), X^- (X=Cl, Br, I) electrode has been used[21] as electrode of second kind (cell B) Since the concentration of the metal ion is controlled through the solubility equilibrium of silver halide, it is effectively an anion-responsive electrode. Use of Ag-AgCl(s) electrode as indicator is precluded above *c* 250 due to relatively higher solubility of silver chloride in molten nitrates ; Ag^+ from the solubility equilibrium may then compete with complexing metal ions, complicating analysis of data[3].

Use of electrode of third kind (cell C), Pd-PdO-MO (*e g.*, M=Cd, Pb) in molten nitrates, responsive to M^{2+} through the solubility equilibria of two insoluble oxides, was first suggested by Inman[22].

Reference electrodes generally used[12] are Ag-Ag^+ and Ag-AgX(s), isolated in a portion of the melt; electrical contact with the solvent is made

† Dedicated to Professor R. C Mehrotra, F. N. A (Former Vice-Chancellor, University of Delhi, Delhi) on his sixtieth birthday.

* To whom correspondence should be addressed.

TABLE 1 – ELECTRODE REACTIONS, EQUATIONS FOR NERNST SLOPES AND ACTIVITY COEFFICIENTS FOR ELECTROCHEMICAL CELLS USED IN THE STUDY OF ASSOCIATION EQUILIBRIA

Cell	Electrode reaction and Nernst equation	Equation for Activity Coefficient (in presence of complexing ion)
II A , Ag^+ | Solvent $AgNO_3$ (R'_{Ag}) || Solvent $AgNO_3, L^{l-}$ (R_{Ag}, R_L) | Ag^+, Ag	$Ag = Ag^+ + e^-$ $E_{cell} = \frac{2.303\ RT}{F} \log \frac{R_{Ag}}{R'_{Ag}}$	$\Delta E†_{cell} = \frac{2.303\ RT}{F} \log R_{Ag} - \frac{RT}{F} N_L$ Second term on the right hand side arising as a result of dilution, is small and has generally been neglected.
II B , $AgX(s)$ | Solvent $AgX(s), X$ (R'_X) || Solvent $M(NO_3)_m, X$ (R_M, R_X) | $AgX(s), Ag$	$Ag + X^- = AgX(s) + e^-$ $E_{cell} = \frac{2.303\ RT}{F} \log \frac{R_X}{R'_X}$	M^{m+} added as $M(NO_3)_m$ $\gamma_{\bar{X}}^{-1} = \exp\left(\frac{\Delta E†_{cell}\ F}{RT}\right)$ M^{m+} added as MX_m $\gamma_{\bar{X}}^{-1} = \left[\frac{R_X + R_{MX_m}}{R_X}\right] \exp\left(\frac{\Delta E†_{cell}\ F}{RT}\right)$
II C , $AgX(s)$ | Solvent $AgX(s), X$ (R'_X) || Solvent $Cd^{2+}/Pb^{2+}, X$ $(RCd^{2+}/Pb^{2+}, R_X)$ | Pd, PdO, CdO/PbO $M = Tl^+, Cd^{2+}, Zn^{2+}, Pb^{2+}$, etc., L is ligand inclusive of X = Cl, Br, I)	$Pd = Pd^{2+} + 2e^-$ $CdO/PbO + Pd^{2+} = PdO + Cd^{2+}/Pb^{2+}$ $CdO/PbO + Pd = PdO + Cd^{2+}/Pb^{2+} + 2e^-$ $E_{cell} = \text{Constant} + \frac{2.303\ RT}{2F} \log R_{Cd/Pb}$	$\log \gamma Cd/Pb = \frac{\Delta E†_{cell}\ F}{S_{expt}}$ S_{expt} is experimental Nernst slope.

† R, T, F have the usual thermodynamic significance, ΔE_{cell} is the difference in emf of the cell in presence and absence of complexing ion

Prime (′) represents concentration units in reference half-cell.

hrough a fine porosity fritted glass disc or an asbestos fibre sealed through a glass diaphragm.

The choice of the concentration units and standard states for a solution depends upon the model employed for the interpretation of solution properties; in molten salts Temkin model[23] has been widely used. For a system containing metal (M^{m+}) and ligand (L^{l-}) ions in the reciprocal charge symmetric (AC+BC) or asymmetric $(AC+B'C_2)$ systems, mol fraction (N_i) of M^{m+} and L^{l-} in terms of mol ratios (R_i, mol of solute per mol of solvent) are[16]

$$N_M^{m+} = \frac{n_M^{m+}}{\Sigma\, n_{cations}} = \frac{R_{M(NO_3)_m}}{1+\left(\frac{1}{p}\right) R_{A_lL} + R_{M(NO_3)_m}} \quad \dots (1)$$

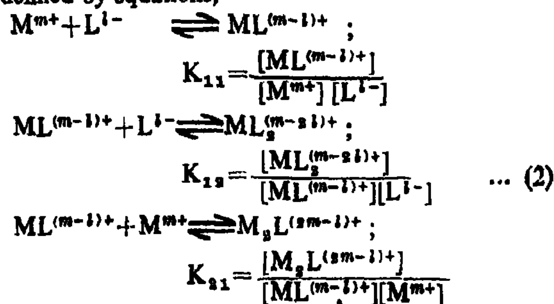
$$N_L^{l-} = \frac{n_L^{l-}}{\Sigma\, n_{anions}} = \frac{R_{A_lL}}{1 + mp\, R_{M(NO_3)_m} + R_{A_lL}}$$

where n_i is the number of mols of the species i; p=1 for the solvent (AC+BC), and $p=(y+1)/(y+2)$ for the solvent $(AC+B'C_2)$, y being the ratio of mols of univalent solvent cations and divalent solvent cations. At $R_i < 10^{-3}$, as is generally employed in these investigations, ion mol ratios are not significantly different from the mol fractions.

Evaluation of Association Constants

Single ligand complexes: Negative deviations from Henry's law in presence of complexing ions have been interpreted due to the formation of associated or complexed species in solution. Thermodynamic association constants and related parameters in molten salts from EMF data have generally been evaluated using the graphical extrapolation method of Braunstein *et al*[4]; computer evaluation method has been employed by Inman *et al*[24] and others[25-28].

Consider a dilute solution containing both M^{m+} and L^{l-} in molten salt mixture (AC+BC) or $(AC+B'C_2)$ as solvent, and assume that M^{m+} and L^{l-} associate to form the species of the type $ML^{(m-l)+}$, $ML_2^{(m-2l)+}$, $M_2L^{(2m-l)+}$ etc. for which corresponding association constants K_{11}, K_{12}, K_{21} *etc.* are defined by equations,



$$M^{m+} + L^{l-} \rightleftharpoons ML^{(m-l)+}; \quad K_{11} = \frac{[ML^{(m-l)+}]}{[M^{m+}][L^{l-}]}$$

$$ML^{(m-l)+} + L^{l-} \rightleftharpoons ML_2^{(m-2l)+}; \quad K_{12} = \frac{[ML_2^{(m-2l)+}]}{[ML^{(m-l)+}][L^{l-}]} \quad \dots (2)$$

$$ML^{(m-l)+} + M^{m+} \rightleftharpoons M_2L^{(2m-l)+}; \quad K_{21} = \frac{[M_2L^{(2m-l)+}]}{[ML^{(m-l)+}][M^{m+}]}$$

Although solutes are generally added as $M(NO_3)_m$ and A_lL, their mol ratios, $<10^{-3}$, do not significantly alter the ratio of two solvent cations.

where the concentrations may be expressed as mol ratios. Expressing the total (stoichiometric) concentrations of the solute components* in the solvent by the mass-balance equations[4,29]:

$$R_M = R_M^{m+} + R_{ML}^{(m-1)+} + R_{ML_2}^{(m-2)+} + 2R_{M_2L}^{(2m-1)+} + \ldots \quad \ldots (3)$$

$$R_L = R_L^{1-} + pR_{ML}^{(m-1)+} + 2pR_{ML_2}^{(m-2)+} + pR_{M_2L}^{(2m-1)+} + \ldots \quad \ldots (4)$$

and defining the activity coefficients of the solutes by equations

$$1/\gamma_M = R_M/R_M^{m+}$$
$$1/\gamma_{SL} = R_L/R_L^{1-}$$

equations for activity coefficients in terms of K_{ij} and R_i are:

$$1/\gamma_M = 1 + K_{11}R_L + K_{11}(2K_{21} - pK_{11})R_LR_M + K_{11}K_{12}R_L^2 + \ldots \quad \ldots (5)$$

$$\ln 1/\gamma_M = K_{11}R_L + K_{11}(2K_{21} - pK_{11})R_LR_M + K_{11}(K_{12} - \tfrac{1}{2}K_{11})R_L^2 + \ldots \quad \ldots (6)$$

$$1/\gamma_{SL} = 1 + pK_{11}R_M + pK_{11}(2K_{12} - K_{11})R_LR_M + pK_{11}K_{21}R_M^2 + \ldots \quad \ldots (7)$$

Association constants using Ag-Ag$^+$ (cell A) or Pd-PdO-CdO/PbO (cell C) indicator electrodes may be evaluated from the relationships based on equation (6), viz.,

$$S_M(0,0) = \lim_{R_M\to 0}[S_M(0)] = \lim_{\substack{R_L\to 0\\ R_M\to 0}}\left[\frac{\partial \ln(1/\gamma_M)}{\partial R_L}\right]_{R_M} = K_{11} \quad \ldots (8)$$

$$\lim_{\substack{R_M\to 0\\ R_L\to 0}}\left[\frac{\partial(1+K_{11}R_M)S_M(0)}{\partial R_M}\right] = 2K_{11}K_{21} \quad \ldots (9)$$

$$\ln(1/\gamma_M) = AR_L + BR_L^2 + \ldots \quad \ldots (10)$$

$$\lim_{R_M\to 0}[B] = [B_0] = K_{11}(K_{12} - \tfrac{1}{2}K_{11}) \quad \ldots (11)$$

For the cell B, using Ag-AgX(s) as indicator electrode, the corresponding equations are

$$S_L(0,0) = \lim_{R_L\to 0}[S_L(0)] = \lim_{\substack{R_L\to 0\\ R_M\to 0}}\left[\frac{\partial(1/\gamma_{SL})}{\partial R_M}\right]_{R_L} = pK_{11} \quad \ldots (12)$$

$$\lim_{R_L\to 0}\left[\frac{\partial S_L(0)}{\partial R_L}\right] = \lim_{\substack{R_L\to 0\\ R_M\to 0}}\left[\frac{\partial^2(1/\gamma_{SL})}{\partial R_L\,\partial R_M}\right] = pK_{11}(2K_{12} - K_{11}) \quad \ldots (13)$$

$$(1/\gamma_{SL} - 1) = AR_M + BR_M^2 + \ldots \quad \ldots (14)$$

$$\lim_{R_L\to 0}[B] = [B_0] = pK_{11}K_{21} \quad \ldots (15)$$

Since functions are extrapolated to zero concentration both in respect of R_M and R_L, association constants are truly thermodynamic parameters.

Limiting slopes $S_M(0)$ or $S_L(0)$ are generally obtained from large scale plots of $\ln(1/\gamma_M)/(1/\gamma_{SL})$ vs R_L/R_M which are rectilinear at low R_i. For such systems (cf. eqn. 7)

$$\lim_{R_L\to 0} 1/\gamma_{SL} = 1 + pK_{11}R_M \quad \ldots (16)$$

or $\ln(1/\gamma_{SL}) = \ln(1 + pK_{11}R_M)$ ... (17)

from which one has

$$\left[\frac{\partial \ln(1/\gamma_{SL})}{\partial R_M}\right]_{R_M} = \frac{pK_{11}}{1 + pK_{11}R_M} \quad \ldots (18)$$

using the thermodynamic relationship,

$$\lim_{R_L\to 0}\left[\frac{\partial \ln(1/\gamma_M)}{\partial R_L}\right]_{R_M} = \lim_{R_M\to 0}\left[\frac{\partial \ln(1/\gamma_{SL})}{\partial R_M}\right]_{R_M} = S_M(0) \quad \ldots (19)$$

it also follows that

$$S_M(0) = \frac{pK_{11}}{1 + pK_{11}R_M} \quad \ldots (20)$$

Equation (20), valid at low solute concentrations, enables evaluation of K_{11} from a single limiting data for a single initial R_M. Values of K_{11} thus evaluated have been reported[7,10,30] to be close to those from the extrapolated data at several initial R_M.

Mixed ligand complexes: These studies have been reported[5,31,32] for mixed silver halides in molten nitrates. Considering the example of chloride-bromide complexes and representing the association constants for single chloride and bromide species (AgX, AgX_2^- and Ag_2X^+) by K_{11}, K_{12} and K_{21}, and K_{11}^*, K_{12}^* and K_{21}^* respectively, β, the mixed association constants for $AgClBr^-$ (at fixed R_{Cl} and varying R_{Br} and vice versa) defined by

$$\beta = R_{AgClBr}/R_{Ag}.R_{Cl}.R_{Br} \quad \ldots (21)$$

may be evaluated from the equation[5,31]

$$\lim_{R_{Cl}\to 0}\left[\frac{\partial S_{Ag}(0,Cl,0)}{\partial R_{Cl}}\right] = \lim_{R_{Br}\to 0}\left[\frac{\partial S_{Ag}(0,0,Br)}{\partial R_{Br}}\right] = (\beta - \beta_{11}\beta_{11}^*)/2.303 \quad \ldots (22)$$

*Subscripts M, L and SL refer to components $M(NO_3)_m$, A_lL and (A, B or B') L respectively.

where $\beta_{11}(=K_{11})$ and $\beta^*_{11}(=K^*_{11})$ are given by

$$S_{Ag}(0,0,0) = \lim \left[\frac{\partial \ln (1/\gamma_{Ag})}{\partial R_{Cl}}\right] = \beta_{11} \quad \ldots (23)$$

Fixed Br $R_{Ag}\to 0$ R_{Ag}, R_{Br}
$R_{Cl}\to 0$
$R_{Br}\to 0$

$$S_{Ag}(0,0,0) = \lim \left[\frac{\partial \ln (1/\gamma_{Ag})}{\partial R_{Br}}\right] = \beta^*_{11} \quad \ldots (24)$$

Fixed Cl $R_{Ag}\to 0$ R_{Ag}, R_{Cl}
$R_{Br}\to 0$
$R_{Cl}\to 0$

Use of digital computer for evaluating association constants from potentiometric data have been reported[26-28]. It involves several cycles of Newton-Raphson iteratic procedure involving ligand-balance equations in least-squares curve-fitting in conjugation with metal-balance equation.

Results and Discussion

Reversible behaviour of different types of indicator electrodes in cells (A) to (C) has been demonstrated (Fig. 1). In view of discrepancy between calculated and observed Nernst slopes with Pd-PdO-CdO/PbO electrode (cell C), considered[22] to

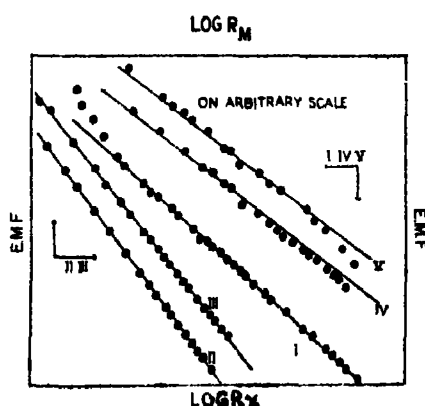


Fig. 1 E M F vs R_M/R_X, in KNO_3-$Ba(NO_3)_2$ ● (Experimental),—(Theoretical), I (Ag-Ag^+), II [Ag-AgBr(s)], III [Ag-AgI(s)], IV (Pd-PdO-CdO), V (Pd-PdO-PbO)

arise due to mixed potential at the electrode surface, experimental slope (S_{expt}), was employed[7,10,25,30,33] instead of that from the Nernst equation $\left(\frac{2.303\ RT}{2\ F}\right)$ in the evaluation of γ_M. In a typical case (Table 2), γ_{gX} (X=Br, I) obtained from CdX_2 addition are consistent[34,35] with the values obtained from $Cd(NO_3)_2$ addition. This establishes usefulness of the latter, where anhydrous solute is difficult to prepare. Typical plots using the extrapolation procedure of Braunstein *et al* are given in Fig. 2. Values of K_{11} ($ML^{(m-1)+}$) and β ($AgClBr^-$) for various systems in different solvents are summarised in Table 3. Data for K_{11} for the same system with different indicator

TABLE 2—COMPARISON OF INTERPOLATED VALUE OF γ^{-1}_{gX} OBTAINED FROM CdX_2 (X=Br, I) AND $Cd(NO_3)_2$ ADDITION

$R_{Cd^{2+}}\times 10^3$	γ^{-1}_{gX} CdX_2 addition	$Cd(NO_3)_2$ addition
(Solvent : $NaNO_3$ – KNO_3 (1 1), Temp = 513.2 K, X = Br, R_{Br} = 1 732 × 10^{-3}, Ref 34)		
0.1195	1 109	1.109
0.2845	1 270	1 268
0 6940	1.687	1 687
0.7655	1 820	1 779
(Solvent . KNO_3 – $Ba(NO_3)_2$ (0 876 0 124), Temp = 568 2 K, X = I, R_I = 9 829 × 10^{-4}, Ref 35)		
0 2499	1 050	1.048
0 7080	1.120	1 110
1 1326	1 220	1 190
1 7319	1 330	1 320

electrodes illustrated for Cd-Br complexes (Fig. 2a) are consistent[7,30]. Also, K_{11} from a single set data (eqn. 20) are seen[7,10,30] (Fig 2b) to be close to those from extrapolation data (eqn. 8) at several initial solute concentrations. A comparison of association constants for Ag-X (X=Cl, Br) complexes in $NaNO_3$-$Ba(NO_3)_2$ from graphical extrapolation and computer evaluation (using one degree fit) for K_{11} is shown in Table 4. The stoichiometric association constants K_{11} are generally comparable. Since several cycles have to be used, the error introduced in evaluating association constants may get accumulated in the higher ones due to which the utility of computer method in evaluating higher association constants is limited. A possible modification would be simultaneous processing of data at various initial solute concentration over a wide range of concentrations.

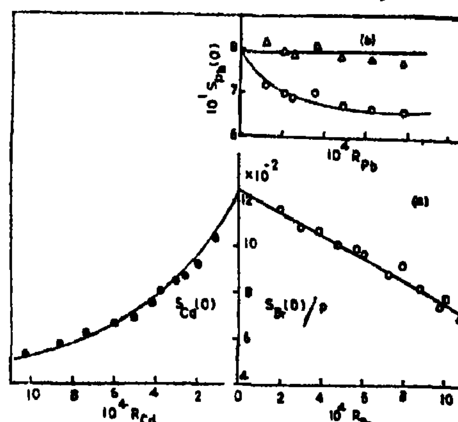


Fig 2 (a) Graphical extrapolation of limiting slopes obtained with Ag, AgBr(s), (O) (Eqn. 12) and Pd-PdO-CdO, (●) (Eqn. 8) electrodes to evaluate K_{11} at 568 2 K.
(b) Graphical extrapolation of limiting slopes to evaluate K_{11} ($PbCl^+$ at 588 2 K using equations 8 (O) and 20 (Δ).

Applicability of quasi-lattice model: From the temperature-dependence of the association constants, specific Helmholtz free energies (ΔA_{ij}), the energy required for the formation of the associated species

TABLE 3 – ASSOCIATION CONSTANTS K_{11} AND SPECIFIC HELMHOLTZ FREE ENERGIES $-\Delta A_{11}$ FOR REACTION $M^{m+} + L^{l-} \rightleftharpoons ML^{(m-l)+}$ IN MOLTEN SALTS*

Complex/Solvent (Composition, Mol %)	Temp range K	Cell used	K_{11}	$-\Delta A_{11}$	Reference
Silver-Chloride					
$NaNO_3$ (100)	(604 – 711)	A	227 – 146	20.3±0.1	38
KNO_3 (100)	623, 709	A	553, 315	24.4±0.1	56
	643, 709	A	415, 270	23.7±0.1	36
	658	A	455	24.7	51
	675, 696	A	330, 290	23.6	57
$CsNO_3$ (100)	713	A	506	27.4	55
$LiNO_3 - KNO_3$ (47 : 53)	498	A	860	21.3	58
(33 : 67)	664	A	380	24.0	55
(30 : 70)	513	A	1090	23.0	59
$NaNO_3 - KNO_3$ (50 : 50)	(506 – 801)	A	1050 – 133	22.4±0.3	51
$KNO_3 - CsNO_3$ (67 : 33)	658	A	530	25.6	55
$KNO_3 - Ca(NO_3)_2$ (80 : 20)	593, 623	A	518, 417	22.9±0.1	47
$KNO_3 - Sr(NO_3)_2$ (80 : 20)	623	A	336	21.9	47
$KNO_3 - Ba(NO_3)_2$ (89 : 11)	(623 – 663)	A	396 – 288	22.4±0.3	60
$NaNO_3 - Ba(NO_3)_2$ (94.2 : 5.8)	(623 – 673)	A	290 – 207	21.1±0.1	61
$Li_2SO_4 - K_2SO_4$ (71.5 : 28.5)	(600 – 700)	A	32 – 27	9.8±1.2	62
Silver-Bromide					
$NaNO_3$ (100)	(675 – 773)	A	633 – 352	27.3±0.1	49
KNO_3 (100)	(676 – 773)	A	932 – 540	29.8±0.4	63
$KNO_3 - Ba(NO_3)_2$ (89 : 11)	(623 – 683)	A	2245 – 783	30.2±1.5	64
$NaNO_3 - Ba(NO_3)_2$ (94.2 : 5.8)	(623 – 673)	A	1888 – 921	30.0±0.8	65
$Li_2SO_4 - K_2SO_4$ (71.5 : 28.5)	650	A	160	18.9	66
Silver-Iodide					
$NaNO_3$ (100)	623	A	49000	47.6	67
KNO_3 (100)	623	A	12000	40.3	67
	675	A	5420	39.2	63
$KNO_3 - NaNO_3$ (80 : 20)	673	A	7000	40.5	67
(50 : 50)	623, 648	A	16000, 13000	41.8±0.6	67
$KNO_3 - Ba(NO_3)_2$ (89 : 11)	(623 – 663)	A	36848 – 8982	43.7±2.4	68
$NaNO_3 - Ba(NO_3)_2$ (94.2 : 5.8)	(623 – 698)	A	8061 – 3109	37.9±0.6	69
$Li_2SO_4 - K_2SO_4$ (71.5 : 28.5)	650	A	1700	31.5	66
Silver-Flouride					
$NaNO_3$ (100)	(586 – 683)	A	$<1^a$	0.4±0.2	70
KNO_3 (100)	(619 – 683)	A	$17-15^a$	7.8±0.1	70
$KNO_3 - NaNO_3$ (33 : 67)	(558 – 663)	A	$\approx 2^a$	1.7±0.1	70
(67 : 33)	(557 – 647)	A	$6-5^a$	0.9±0.1	70
Silver-Cyanide					
$NaNO_3 - KNO_3$ (50 : 50)	(519 – 599)	A	230000 – 190000	49.4±3.1	71
Silver-Phosphate					
$NaNO_3 - KNO_3$ (50 : 50)	(524 – 622)	A	$665-579^b$	23.0±1.7	45
Silver-Nitrite					
$NaNO_3 - KNO_3$ (50 : 50)	(523 – 623)	A	31 – 13	7.5±1.0	42

(Table 3 contd.)

(Table 3 Contd.)

Complex/Solvent (Composition, Mol %)	Temp. range K	Cell used	K_{11}	$-\Delta A_{11}$	Reference
Silver-Iodate					
$NaNO_3-KNO_3$ (50 : 50)	(524–622)	A	24–26[b]	8.6±0 9	44
Silver-Molybdate					
$LiNO_3$ (100)	(541–622)	A	12–10[a]	5.6±0.1	41
$NaNO_3$ (100)	(584–690)	A	41–26[a]	10 6±0 1	41
KNO_3 (100)	(619–714)	A	72–52[a]	14 3±0.1	41
$LiNO_3-NaNO_3$ (60 : 40)	(566–650)	A	15–13[a]	6 8±0 3	41
$LiNO_3-KNO_3$ (43 : 57)	(549–653)	A	21–16[a]	7 6±0.3	41
$NaNO_3-KNO_3$ (50 : 50)	(517–646)	A	67–56[a]	11 7±0 3	41
	(524–622)	A	60–44[b]	11 7±0 5	46
Silver-Chromate					
$LiNO_3$ (100)	(528–600)	A	8–7[a]	4 4±0.1	8
$NaNO_3$ (100)	(584–673)	A	31–25[a]	9 8±0 2	8
KNO_3 (100)	(615–675)	A	52–44[a]	12 5±0 3	8
$LiNO_3-NaNO_3$ (60 : 40)	(519–610)	A	14–12[a]	5 7±0 4	8
$LiNO_3-KNO_3$ (43 57)	(429–595)	A	22–15[a]	6 5±0 5	8
$NaNO_3-KNO_3$ (50 · 50)	(580–695)	A	47–28[a]	10 9±0 5	8
	(524–622)	A	43–35[b]	10.4±0.5	43
Silver-Sulphate					
$NaNO_3$ (100)	(594–684)	A	≈1[a]	0 9±0 2	41
KNO_3 (100)	(622–715)	A	13–10[a]	6 6±0 2	41
	(636–706)	A	13–12	7 2±0 8	72
	(622–703)	A	≈13	7 1±0 4	73
$NaNO_3-KNO_3$ (50 . 50)	(526–685)	A	4–3[a]	2 3±0 3	41
Silver-Mixed Halide (Cl+Br)					
$NaNO_3$ (100)	711	A	53000	54 8	5
Cl : Br 2 : 1	663, 723	A	414, 278	24 3±0 1	32
Cl · Br 1 · 2	663, 723	A	627, 407	26 6±0 1	32
$NaNO_3-Ba(NO_3)_2$ (94 2 : 5.8)	(623–673)	A	340250–98527	56 6±1 2	31
$KNO_3-Ba(NO_3)_2$ (89 11)	623, 663	A	889020,341866	62 5±0 1	74
	643, 683	A	595815,187920	60 6±0 8	75
Cadmium-Chloride					
$LiNO_3-KNO_3$ (50 50)	(413–473)	B	1850–1200	21 4±0 2	48
(40 · 60)	453	B	1500	21 5	48
(60 40)	453	B	1300	21 0	48
(43 . 57)	425	B	1795	20 8	76
$NaNO_3-KNO_3$ (50 : 50)	527	C	842[b]	22 5	25
$KNO_3-Ba(NO_3)_2$ (87.6 : 12.4)	(568–628)	C	600–450	23.2±0 4	33
Cadmium-Bromide					
$LiNO_3-KNO_3$ (26 : 74)	513	B	2300	26 2	48
(40 : 60)	513	B	2650	26.7	48
(50 : 50)	(444, 513)	B	8000, 3200	27 4±0 2	48
(65 : 35)	513	B	3600	28 1	48
(80 : 20)	513	B	4200	28 7	48
$NaNO_3$ (100)	604	C	625	24.3	7
KNO_3 (100)	631	C	650	25 6	7

(Table 3 Contd.)

(Table 3 Contd.)

Complex/Solvent (Composition, Mol %)	Temp. range K	Cell used	K_{11}	$-\Delta A_{11}$	Reference
$NaNO_3-KNO_3$					
(50 : 50)	531	C	1500	25.2	7
	527	C	1983[b]	26.2	25
	513, 573	B	1520, 990	24 4±0 8	21
(53 : 47)	(529–571)	B	1167–810[b]	24 0±0 2	77
$NaNO_3-LiNO_3$					
(50 : 50)	513	B	2700	26 8	34
$NaNO_3-Ca(NO_3)_2$					
(67 : 33)	533	B	2400	27 4	29
$KNO_3-Ca(NO_3)_2$					
(67 : 33)	(473–553)	B	(5200–2067)	27 6±0.3	29
$KNO_3-Ba(NO_3)_2$					
(87·6 : 12 4)	(568–608)	B	1281–1135	26 9±0.7	30
	568, 628	C	1260, 1000	26 9±0 8	30
Cadmium-Iodide					
$NaNO_3-KNO_3$					
(50 : 50)	513, 563	B	5330, 3130	30 0±0.3	21
$KNO_3-Ba(NO_3)_2$					
(87.6 : 12 4)	(568–608)	B	4215–3288	32 3±0 5	35
Lead-Chloride					
$LiNO_3-KNO_3$					
(50 : 50)	(433–473)	B	250–205	14 4±0 3	48
$KNO_3-Ba(NO_3)_2$					
(87 6 : 12 4)	(588–628)	C	79–69	13 9±0.2	10
Lead-Bromide					
$NaNO_3-KNO_3$					
(53 : 47)	(528–592)	B	199–122[b]	16 2±0 3	77
(75 : 25)	553, 573	B	180, 160	16 6±0 1	52
(50 : 50)	(513–573)	B	250–170	16 8±0 1	52
(25 : 75)	553,573	B	200, 175	17 1	52
$LiNO_3-KNO_3$					
(50 : 50)	433, 473	B	990, 730	19 3±0 3	48
$KNO_3-Ba(NO_3)_2$					
(87.6 : 12 4)	(568–608)	B	169–137	16 9±0 1	10
Lead-Iodide					
$KNO_3-Ba(NO_3)_2$					
(87 6 : 12 4)	(568–608)	B	3687–2383	31 1±0.1	10
Thallium-Bromide					
$NaNO_3-KNO_3$					
(50 : 50)	513	B	31	84	34
$LiNO_3-KNO_3$					
(40 : 60)	553	B	56	115	78
Cobalt-Cyanide					
LiCl-KCl					
(59 : 41)	723	A	435[b]	26 9	79
Platinum-Bromide					
LiCl-KCl					
(59 : 41)	723	A	24[b]	10 6	79
Copper-Cyanide					
LiCl-KCl					
(59 : 41)	643	A	4372[b]	36 22	79

* K_{11} in (mol/mol of solvent)$^{-1}$, and ΔA_{11} in kJ mol^{-1} for Z = 5

[a]Based on quasi-lattice model equation (25).

[b]Converted into mol/mol basis from molality unit.

$M_iL_j^{(im-jl)+}$ may be generalised using the quasi-lattice model equations[86-88] :

$$K_{11}=Z\,[\exp(-\Delta A_{11}/RT)-1] \quad \dots (25)$$

$$K_{12}=\frac{Z-1}{2}\left[\exp(-\Delta A_{12}/RT)-1+\frac{\exp(-\Delta A_{12}/RT)-\exp\left(\frac{-\Delta A_{11}}{RT}\right)}{\exp(-\Delta A_{11}/RT)-1}\right] \quad \dots (26)$$

$$K_{21}=\frac{Z-1}{2}\left[\exp(-\Delta A_{21}/RT)-1+\frac{(-\Delta A_{21}/RT)-\exp\left(\frac{-\Delta A_{11}}{RT}\right)}{\exp(-\Delta A_{11}/RT)-1}\right] \quad \dots (27)$$

Here Z is the quasi-lattice coordination number

TABLE 4 — COMPARISON OF ASSOCIATION CONSTANTS OF Ag–X (X = Cl, Br) COMPLEXES EVALUATED BY GRAPHICAL AND COMPUTER METHOD IN $NaNO_3-Ba(NO_3)_2$

Temp/K	K_{11} (Graphical)	K_{11} (Computer one-degree fit)
	Silver-Chloro complexes (Ref 28, 60)	
623.2	290 ± 14	292 ± 22
648.2	249^{+9}_{-12}	241^{+29}_{-28}
673.2	207^{+23}_{-27}	198^{+20}_{-19}
	Silver-Bromo complexes (Ref. 28, 65)	
623.2	1888^{+70}_{-46}	1882^{+450}_{-441}
648.2	1474^{+46}_{-92}	1290^{+165}_{-178}
673.2	921^{+92}_{-46}	821^{+126}_{-96}

generally taken[2] between 4 to 6, and $\Delta A=\Delta\epsilon-T\Delta S^{int}$ in which $\Delta\epsilon$, the association energy is temperature-independent and $\Delta S^{int}=d(-\Delta A)/dT$ accounts[36] for any variation of the internal degrees of freedom of the species taking part in the association processes.

Applicability of the quasi-lattice model containing monovalent and divalent cations and single and polyatomic anions (mixed ligand) has been reported (Table 3); for mixed solvent, ΔA_{mix} is given by temperature independent linear equation[39]

$$\Delta A_{mix}=Y\,\Delta A_{AC}+(1-Y)\,\Delta A_{BC/B'C_2} \quad \dots (28)$$

(Y is mol fraction of AC)

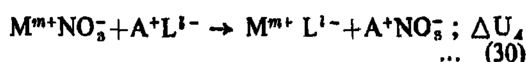
In some of the systems (Table 3), ΔA_{11} are found to be temperature dependent; non-zero values of $\left(-\frac{d\,\Delta A}{dT}\right)$ has been ascribed[38] to vibrational entropy contributions *etc.* For Ag-CrO_4 complexes, it is reported[8] that ΔA values are temperature-invariant in single solvents, but show a marked dependence in mixtures. This difference in thermodynamic behaviour of ternary and quaternary systems, has led to modification of quasi-lattice formulation using a non-linear equation[40] for ΔA_{mix} given by

$$\Delta A_{mix}=RT\ln\left[Y\exp(\Delta A_{AC}/RT)+(1-Y)\exp(\Delta A_{BC/B'C_2})/RT\right] \quad \dots (29)$$

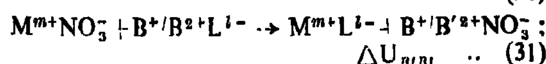
which has been applied to silver-sulphate[41], silver-molybdate[41] and silver-chromate[8] complexes in molten nitrates.

Recently, Holmberg *et al*[42-46] examined the applicability of the quasi-lattice model involving polyatomic oxoanion ligands. In these cases also temperature-dependence of the association constants is not described by the quasi-lattice formulation. Relatively small values of ΔA for the formation of $AgNO_3$[42] compared to that for chromate[43], iodate[44], phosphate[45] and molybdate[46] has been ascribed to the fact that Ag coordinates to nitrogen[48]; for others cordination occurs through oxygen.

Solvent effect: Precise data on association constants and specific Helmholtz free energies are available only in relatively fewer single and mixed molten nitrates. The influence of the presence of $BC/B'C_2$ in the solvent mixture $(AC+BC)/(AC+B'C_2)$ on the stability of M-L band has generally been considered in terms of the 'reciprocal coulomb effect'[47-49]; it results in stabilisation of the pair of oppositely charged ions with the highest charge density. For a system consisting of ions having the same charge, the pairs of smaller ions and pairs of bigger ions of opposite charges will be more stable relative to pairs of ions of mixed size. Considering the change of coulombic energy in the exchange of nearest neighbours taking place in the association reactions of M^{m+} and L^{l-} in solvents AC and $BC/B'C_2$,



$$M^{m+}NO_3^-+A^+L^{l-}\rightarrow M^{m+}L^{l-}+A^+NO_3^-\ ;\ \Delta U_A \quad \dots (30)$$



$$M^{m+}NO_3^-+B^+/B^{2+}L^{l-}\rightarrow M^{m+}L^{l-}+B^+/B'^{2+}NO_3^-\ ;\ \Delta U_{B/B'} \quad \dots (31)$$

The energy difference, $\Delta(\Delta U)$ in the two pure solvents would be given by the relation

$$\Delta(\Delta U)=\Delta U_{B/B'}-\Delta U_A = -Ne^2\left[\frac{1}{r_A+r_L}+\frac{1}{r_{B/B'}+r'_{NO_3}}-\frac{1}{r_A+r_{NO_3}}-\frac{2}{r_{B/B'}+r_L}\right] \quad \dots (32)$$

where r_i is the ionic radius, N, the Avogardo's number and *e* the electronic charge.

For alkali metal nitrates, stability of chloro and bromo complexes in fused alkali nitrates in the order, Li < Na < K < Cs, and that for iodo complexes in the reverse order is observed, iodide being larger than nitrate. The expected trend in mixed nitrate systems relative to single nitrates is shown for Ag-X[49-51], Cd-X[7,52] and Pb-X[52] (X = Cl, Br) complexes in $NaNO_3-KNO_3$. For Cd-Br complexes, the order of stabilisation is $Ba^{2+} > Ca^{2+} > Li^+$, while destablisation, due to the presence of Na^+, is observed[50] and for Pb-Br complexes[10], the magnitude of destablisation is in the order $Ba^{2+} > Na^+$, while presence of Li^+ causes stabilisation in KNO_3-BNO_3 ($B=Ba^{2+}, Ca^{2+}, Li^+, Na^+$), in which both the direction and magnitude of stabilisation are different from those predicted from reciprocal-coulomb effect. This anomalous behaviour also seen in other solvents has been ascribed to the neglect of the long range coulombic[52], dispersion and polarisation energies[2,34,53] and also the difficulty of assigning[47] an effective ionic radius to the nitrate ion.

For the mixed ligand species, the equlibrium

constants given by

$$\text{equilibrium constant} = \beta/(\beta_{12}\,\beta^{*}_{12})^{1/2} \quad \cdots \quad (33)$$

for the exchange reaction $\frac{1}{2}\,AgCl_2^- + \frac{1}{2}\,AgBr_2^- \rightleftharpoons AgClBr^-$ have been evaluated[5,31]; values are generally higher than the statistical value 2. The stabilisation of the mixed complex over and above the statistical value has been considered to arise due to the electrostatic effect of the exchange of ligands and to the polarizability of the central ion[33,34]. Also the values of β_{11} and β^{*}_{11} for single halides evaluated from these (mixed halide) studies generally agree[5,31] with those independently done for single halide under similar conditions.

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Reactions of Benzotelluracyclopentane Diiodide

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Benzotelluracyclopentane diiodide (I) and the derivatives of the general formulae $C_8H_8TeX_2$ (X = halide, pseudohalide, carboxylate) and $[R_4N]^+[C_8H_8TeI_2X]^-$ (R = alkyl; X = halide) have been synthesized and characterized I reacts with $Na_2S \cdot 9H_2O$ to give C_8H_8Te which undergoes oxidative addition reactions yielding C_8H_8TeXY (XY = halogen, interhalogen, organic halide, N-bromosuccinimide or benzamide) and molecular adducts with $HgCl_2$ and Cu_2Cl_2 Te-C (alkyl) and Te-N bonds are readily cleaved by electrophiles The elemental analysis, molar conductance, uv, ir, pmr and tga data are presented in support of the structure of newly synthesized compounds

HETEROCYCLIC organotelluriums have recently been a subject of detailed investigation[1-8] In continuation to our studies on the chemistry of organometallic compounds of tellurium[9-12], we report the synthesis and reactivity of benzotelluracyclopentane diiodide under varying conditions

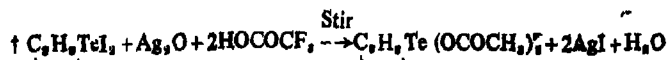
Experimental

Materials and methods : α-α'-Dibromoxylene[13], IBr[14] $(SCN)_2$[15] and Cu_2Cl_2[16] were prepared by the reported methods Silver salts were freshly prepared before use Tetraalkylammonium salts, mercuric chloride and iodine monochloride of BDH grade were used All the physico-chemical measurements were made as reported earlier[6]. TGA was recorded on an apparatus designed by Fertilizer Corporation of India

(A) *Preparation of benzotelluracyclopentane diiodide (I)* · Finely powdered tellurium metal (200 mesh) (2 54 g ; 20 mmol), sodium iodide (12 g ; 80 mmol) and α-α'-dibromoxylene (5.2 g ; 20 mmol) in 2-methoxyethanol (~100 ml) were stirred at 100-110° for 2 hr Addition of deionized water yielded an orange precipitate which was recrystallized with hot 2-methoxyethanol, washed with acetone (~15 ml) and dried *in vacuo* (yield=8 25 g ; 85%).

TABLE 1—EXPERIMENTAL DATA OF $C_8H_8TeX_2$

Compound $C_8H_8TeX_2$ X	Method	Colour (m p °C)	Analysis : Found (Calcd) Te	X	C	H	N	Molar conductance ($10^{-3}M$ soln in acetone) $\Lambda^{-1}cm^2mol^{-1}$
I	A	Yellow orange (225d) Orange red (222d)	26 10 (26 28)	52 13 (52 27)	19 48 (19 79)	1 68 (1 66)	–	7.31
Cl	B	White (240d)	42 10 (42 16)	23 28 (23 43)	31 05 (31 75)	2 34 (2 67)	–	5 78
Br	B	Yellow (219d)	32 36 (32.59)	40 50 (40.81)	24 34 (24 54)	2 08 (2 06)	–	4 96
CN	B	White (140d)	45.00 (44.96)	–	42 05 (42 32)	2 66 (2 84)	9 67 (9 87)	6.31
NCO	B	White (82d)	40 24 (40.41)	–	38.00 (38 04)	2 45 (2 56)	8 68 (8 87)	5.14
NCS	B	White (117d)	36 23 (36 68)	–	34.42 (34.52)	2 15 (2.32)	8.00 (8.05)	8.45
NCSe	B	Dark yellow (119)	28.95 (28.90)	–	27 09 (27.20)	1 77 (1.83)	6.16 (6.34)	7.71
CH_3COO	B	White (168)	36.25 (36 47)		41.12 (41 20)	4.00 (4.03)	–	9.91
CH_2ClCOO	B	White (119-22)	30.42 (30 47)	–	34.28 (34.42)	2 69 (2 89)	–	9.25
CF_3COO	†	White (159)	27.80 (27.87)	–	31.62 (31.48)	1.83 (1.76)	–	8.67
C_6H_5COO	B	White (162)	26.85 (26.92)	–	55.52 (55.75)	3.91 (3.83)	–	7.31



† $C_8H_8TeI_2 + Ag_2O + 2HOCOCF_3 \xrightarrow{Stir} C_8H_8Te(OCOCH_3)_2 + 2AgI + H_2O$

(B) *Preparation of benzotelluracyclopentane dichloride* : A solution of compound (I) (0.970 g ; 2 mmol) in acetone (25 ml) was stirred with silver chloride (1 g ; > 4 mmol). The insoluble silver salts were filtered off and the excess solvent distilled off under reduced pressure On standing overnight in deep freeze, white crystalline benzoteluracyclopentane dichloride was obtained. It was washed with petroleum ether and dried *in vacuo* (yield=0 483 g ; 80%)

(C) *Preparation of* $[Et_4N]^+[C_8H_8TeI_2Cl]^-$: A solution of compound (I) (0.970 g ; 2 mmol) in acetonitrile (20 ml) was mixed with a solution of tetraethylammonium chloride (0 662 g ; 4 mmol) in acetonitrile (20 ml). The mixture was refluxed for ~ 4 hr. The reaction mixture on concentration to crystallisation yielded the desired complex as a yellow solid. It was washed with petroleum ether and dried *in vacuo* (yield=1.066 g ; 82%).

The experimental details, characterization data and exchange or addition reactions products are summarized in Tables 1 and 2.

Preparation of benzotelluracyclopentane (II) : A mixture of compound (I) (1 94 g ; 4 mmol) and $Na_2S \cdot 9H_2O$ (15 g , ~ 60 mmol) was stirred at 100° for about an hour The mixture was cooled and treated with crushed ice. A mixture of the desired product and unreacted tellurium was obtained. Its solvent ether extract containing the desired product was dehydrated with fused calcium chloride and used *in situ* for further reactions under nitrogen.

Oxidative addition reaction of organotelluride with methyl iodide : An etherial solution of compound(II) (0.92g , 4 mmol) was mixed with methyl iodide (3 ml) and allowed to stand for 48 hr at room temperature. The mixture deposited a yellow crystalline solid which was separated and stored in fresh ether for ~ 12 hr.

TABLE 2—EXPERIMENTAL DATA FOR $[R_4N]^+ [C_8H_8TeI_2X]^-$

Compound $[R_4N]^+ [C_8H_8TeI_2X]^-$ R	X	Method	Colour (m p °C)	Analysis Found (Calcd)% Te	I_2X	C	H	N	Molar conductance ($10^{-3}M$ Soln. in acetonitrile $A^{-1}cm^{-2}mol^{-1}$)
Me	Br	C	Orange (241)	19 90 (19.95)	52 08 (52 17)	22.48 (22 53)	3.08 (3 15)	2 03 (2 19)	173.50
Et	Cl	C	Yellow (177)	19 05 (19.59)	44 30 (44.42)	29 36 (29.51)	4 05 (4.33)	2 02 (2.15)	150.87
Et	Br	C	Yellowish orange (185)	18 18 (18 34)	47.52 (47 97)	27 55 (27 62)	4 00 (4 06)	2.00 (2 01)	144 58
Bu	Br	C	Yellowish orange (202d)	15 40 (15.79,	41 90 (41 30)	35 40 (35.68)	5 32 (5 49)	1 58 (1.73)	177.95

TABLE 3—EXPERIMENTAL DETAILS OF BENZOTELLURACYCLOPENTANE DERIVATIVES

Reaction of C_8H_8Te with XY	Product	Reaction condition (time)	Solvent used in reaction	% Yield	Colour	m p. (°C)
I_2	$C_8H_8TeI_2$	r. temp (1/2 hr)	Solvent ether	95	Orange	221 d
Br_2	$C_8H_8TeBr_2$	0°C(1 hr)	„	90	Yellow	216 d
ICl	C_8H_8TeICl	~5°C(1 hr)	„	45	Dirty yellow	231
IBr	C_8H_8TeIBr	~5°C(1 hr)	„	85	Brownish yellow	212 d
$(SCN)_2$	$C_8H_8Te(SCN)_2$	~20°C(3 hr)	Solvent ether and CCl_4	66	White	118 d
*MeI	$C_8H_8Te\langle^{Me}_{I}$	r. temp. (48 hr)	Solvent ether	89	Yellow	214
$Br-N\langle C(=O), C(=O) \rangle$	$C_8H_8Te(Br)N\langle C(=O), C(=O) \rangle$	r. temp. (2 hr)	Solvent ether and benzene	85	White	145
$BrNHCOC_6H_5$	$C_8H_8Te\langle^{Br}_{NHCOC_6H_5}$	„	„	83	White	125
$HgCl_2$	$C_8H_8Te.HgCl_2$	r. temp. (1/2 hr)	Solvent ether and water	95	White	185
Cu_2Cl_2	$(C_8H_8Te)_2.Cu_2^{s}Cl_2$	„	Solvent ether and 1*M*HCl	90	Dirty white	165

Note : The observed elemental analysis are in close agreement with that of calculated values* 1 : 1 electrolyte (111.38 Λ^{-1} cm^2 mol^{-1}) in DMF while others are non electrolytes.

TABLE 4—CLEAVAGE REACTIONS OF Te–C AND Te–N BONDS

Compound	Electrophile used	Product	Reaction condition (time)	Solvent used	%Yield	m.p.°C
C_8H_8TeMeI	I_2	$C_8H_8TeI_2$	r. temp (2 hr)	Chloroform	80	218
	IBr	C_8H_8TeIBr	0°C (4 hr)	"	70	210
C_8H_8Te	Br_2	$C_8H_8TeBr_2$	r temp (2 hr)	CCl_4	70	212

It was then filtered, washed with solvent ether and dried *in vacuo* (yield=1.33 g, 89%). The experimental details are summarized in Table 3.

Addition reaction of organotelluride with metal halides: To an etherial solution of compound (II) (0.92 g; 4 mmol) a saturated aqueous solution of $HgCl_2$(1.09 g; 4 mmol) was added dropwise with constant stirring during ½ hr. The precipitated white solid was filtered and dried *in vacuo* over P_2O_5 (yield=1 g; 95%).

The product of reaction of Cu_2Cl_2 in 1*M* HCl with C_8H_8Te was isolated similarly.

Some cleavage reactions: In a representative experiment, a solution of IBr (0.414 g; 2 mmol) in chloroform (15 ml) was added dropwise to a solution of C_8H_8TeMeI (0.756 g; 2 mmol) in chloroform (20 ml) at 0° till no more of it was decolourised. After complete addition, the solution was distilled off under reduced pressure and addition of excess petroleum ether yielded a brownish yellow product which was washed with petroleum ether and dried *in vacuo* and identified as $C_8H_8Te\langle^{I}_{Br}$.

The relevant experimental details of cleavage reactions are summarized in Table 4.

Results and Discussion

The synthesis and reactivity of benzotelluracyclopentane diiodide were examined as follows. The benzotelluracyclopentane diiodide (I) is obtained by interaction of dibromoxylene with a mixture of tellurium metal and sodium iodide (reaction i):

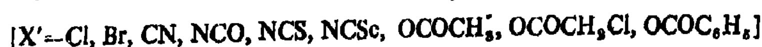


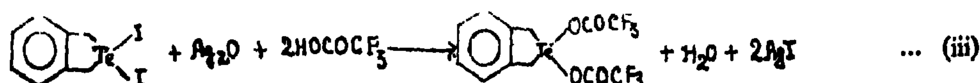
... (i)

The derivatives of compound (I) of the type $C_8H_8TeX_2$ are prepared by the following exchange reactions (ii) and (iii):



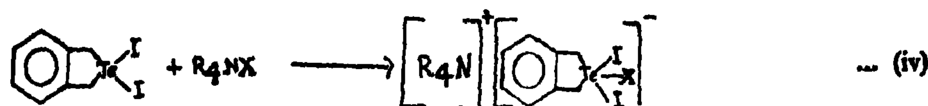
... (ii)


[X'=Cl, Br, CN, NCO, NCS, NCSe, $OCOCH_3$, $OCOCH_2Cl$, $OCOC_6H_5$]



... (iii)

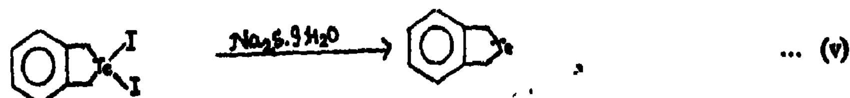
The trihalo anionic complexes of the type $[R_4N]^+[C_8H_8TeI_2X]^-$ are obtained as follows (iv):



... (iv)


[R=Me, Et, Bu; X=Cl, Br]

The compound (I) reacts with $Na_2S.9H_2O$ to give C_8H_8Te [compound (II)] reaction (v):

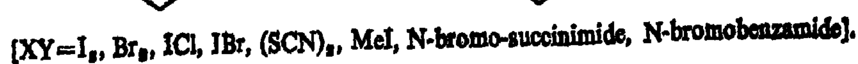


... (v)

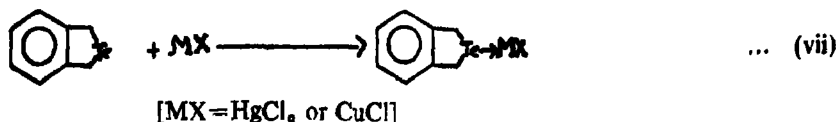
The benzotelluracyclopentane, C_8H_8Te, undergoes several oxidative addition reactions yielding a number of hitherto unknown compounds (reaction vi):



... (vi)


[XY=I_2, Br_2, ICl, IBr, $(SCN)_2$, MeI, N-bromo-succinimide, N-bromobenzamide].

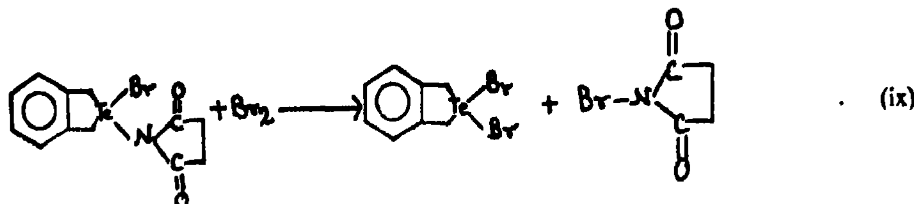
The telluride also reacts with metal halides and yields molecular adducts (reactions-vii) :



$[MX=HgCl_2$ or $CuCl]$

The cleavage of Te-C (alkyl) and Te-N bond in methyl benzotelluracyclopentane iodide and benzotelluracyclopentane bromide succinimide respectively occurs readily with I_2, IBr and Br_2 (reaction viii and ix) :





The Te-C bond in telluracyclopentane diiodide is stable towards halogens and pseudohalogens[8] In the present investigation, the Te-C bond is readily cleaved in methyl benzotelluracyclopentane iodide by electrophiles $XY'(XY'=I_2$, IBr). The Te-N bond in benzotelluracyclopentane bromide succinimide is cleaved in preference to Te-C bond by Br_2

Benzotelluracyclopentane diiodide and its derivatives are stable solids excepting diisothiocyanate, dicyanate and trifluroacetate derivatives which slowly decompose on standing. They are soluble in common organic solvents and are unaffected by atmospheric oxygen and moisture.

The molar conductance ($10^{-3}M$ solution) data presented in Tables 1 and 2 indicate that organotelluriums of the formula $C_8H_8TeX_2$ are non electrolytes while its trihalo anionic complexes possess 1 : 1 electrolytic nature The conductance data in Table 3 indicate that all oxidative addition products are nonelectrolytes excepting C_8H_8TeMeI which is a 1 : 1 electrolyte in DMF.

IR spectra : In the ir spectra of benzotelluracyclopentane derivatives the νTe-C invariably occurs around $\sim 550\ cm^{-1}$, this position being similar to that in telluracyclopentane and telluracyclohexane derivatives[4,5]. νTe-Cl is identified at $282\ cm^{-1}$ and is in agreement with the reported value for $C_4H_8TeCl_2$[5]. $\Delta\nu COO=(\nu_{asy}COO-\nu_{sym}COO)$ for diacetate, dimonochloroacetate, ditrifluoroacetate, dibenzoate are 345, 340, 405 and $298\ cm^{-1}$ respectively which are in close agreement to the reported values for other organotellurium carboxylates[8,9,18] having ester like structure. In almost all the carboxylates $\nu_{asy}COO$ undergoes splitting indicating non equivalence of the carboxylate groups[5,18].

In the newly synthesised chalcogenates NCX (X=O, S, Se), $\nu C-X$ appears at 1305, 862 and 610 for X=O, S and Se respectively showing the pseudohalides groups[19] in the *iso* form In benzotelluracyclopentane dicyanide νCN at $2150\ cm^{-1}$ suggests the presence of normal CN group in the compound[4,5].

The benzamide and succinimide derivatives show characteristic absorptions associated with ν_{asy} CO and ν_{sym}CO modes at 1688 ± 26 and $1290\ cm^{-1}$ respectively[20].

^1H NMR spectra : ^1H NMR spectrum of benzotelluracyclopentane diacetate shows two singlets, one at 1.81 ppm due to methyl protons of acetate groups and the other at 4 36 ppm due to $-CH_2$-Te protons. The multiplet in the range of 7 33-7.0 ppm is attributed to four phenyl protons

In the ^1H NMR spectrum of the complex anion $[(CH_3CH_2)_4N]^+ [C_8H_8TeI_2Cl]^-$ appearance of one multiplet in the range 7 33-7.0 ppm is due to phenyl protons and a quartet at 4 70-3.90 ppm is due to CH_2-Te protons A triplet at 1.36-1 05 ppm and a quartet at 3 40-3 09 ppm are due to $-CH_3$ and $-CH_2$ protons of $[(CH_3CH_2)_4N]^+$ respectively

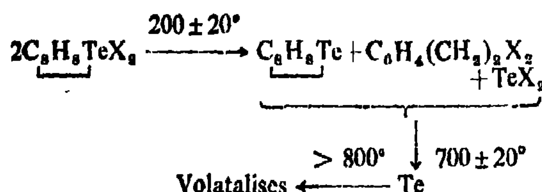
The ^1H NMR spectrum of methyl benzotelluracyclopentane iodide shows three signals, one as a sharp singlet at 2.44 ppm due to Te-CH_3 protons and a quartet at 5 10-4.10 ppm due to Te-CH_2 protons. The phenyl protons appear as a multiplet at 7.13 ppm

The spectra and the integration correspond to the proposed stoichiometry of the compounds.

UV spectrum : The absorption band at 218 nm in the uv spectrum of $C_8H_8TeI_2$ appears at almost identical position (211 nm) as in the spectrum of

$\underline{C_8H_8}Te\,(OCOC_6H_5)_2$. It is attributed to $\pi-\pi^*$ benzoid transition[21].

TGA analysis: The thermogravimetric curves of the two representative compounds $\underline{C_8H_8}TeX_2$ (X= $OCOCH_3$; $OCOC_6H_5$) qualitatively show the following mode of decomposition It starts at 200 ± 20° and at 700 ± 20°, there is a residual mass corresponding to tellurium metal, which volatalises about above 800°.



Biocidal activity. The reaction products of exchange reaction and additions reaction were screened against different microorganism [*E. coli*, *S typhi*, *B. subtilis*, *S. aureus*, *M tuberculosis*, *A terreus*] and showed significant activity. The details of the results obtained will form the subject matter of another paper.

Acknowledgement

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On the Polarographic Reduction Mechanism of Some Heterocyclic Compounds

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For evaluating the mechanistic steps, position at d.m.e and assigning inner or outer sphere path of electrode processes of a number of pyrazole derivatives, thiazoles and their precursors experiments were carried out in the absence and presence of surfactants. All the compounds gave diffusion-controlled, irreversible waves over the entire pH range (2.0-11.0) studied. In presence of surfactants also, diffusion-controlled but more irreversible waves were obtained. In absence and presence of surfactant (CTAB) values of K_{app} and α_{app} for all these compounds were calculated and have been taken as a proof of inner sphere or outer sphere path of the electrode reaction. Results have been explained on the basis of formation of phenylazo-functionalised surfactant as an intermediate species

THE electrochemical reaction at an electrode may either take place in the close vicinity of the electrode or a little far off from the electrode surface. In physico-chemical terminology the former are named as reactions in the 'Inner Helmholtz Plane' (IHP) and the latter as reactions in the 'Outer Helmholtz Plane' (OHP). Generally speaking substances which are easily reducible get reduced in the OHP while difficultly reducible species are reduced in the IHP.

Anson and co-workers[1,2] for the first time attempted to distinguish between IHP and OHP reduction paths in the case of Cr(III) cyanogen complexes. According to them since inorganic ions are easily hydrated or solvated they do not get adsorbed at the electrode and, therefore, undergo reduction easily. On the other hand complexes such as dichromium complexes, which show fair tendency to adsorb, do so by inner sphere path. This distinction can be very well evaluated by carrying out reduction studies in the presence of strongly adsorbable substances.

Literature survey revealed that such studies have not been undertaken with organic compounds. A large majority of compounds, unless they have got a strong lyophilic end group, are adsorbed at the electrode surface and would very likely, show IHP reduction path.

Recently we have reported[3-8] the polarographic reduction of a number of heterocyclic compounds without evaluating the mechanistic steps and their respective position at the d.m.e. Moreover assigning inner or outer sphere path to a variety of compounds would also help in explaining the comparative ease of reduction in various series of compounds.

Keeping in view the importance of the various parameters for distinguishing the two types of mechanistic path, we have considered the following series of compounds :

(i) Coupled products of aryldiazonium chlorides with β-ketoesters, which are precursors of various biologically important compounds.

(ii) 2-Benzothiazolylhydrazono ethyl-2-cyanoethanoates.

(iii) 4-Arylhydrazono - N'-phenylthiocarbamoyl-3-methyl-2-pyrazolin-5-ones

(iv) N'- Phenylthiocarbamoyl-3,5- dimethyl-4-arylazopyrazloes, and

(v) N'-Phenyl-3,5-dimethyl-4-arylazopyrazoles.

Further confirmation in this respect has been made available by considering corresponding data in the presence of surfactants.

Experimental

Five series of compounds including precursors of various heterocycles, coupled products of aryldiazonium chlorides with β-ketoesters, hydrazono compounds (viz., 2-benzothiazolylhydrazono, 2-cyanoethanoates, pyrazolin-5-ones) and azo compounds (phenylazothiocarbamoylpyrazoles, phenylazopyrazoles) were synthesised by literature methods[9-12]. All the compounds were recrystallised from ethanol and their structural characteristics were confirmed by chemical and spectral analysis.

The stock solutions of concentration $1.0 \times 10^{-3} M$ of all the compounds were prepared in methanol. Britton-Robinson buffer in the pH range 2.0 to 11.0 and 1.0 M KCl, 0.01 M cetyltrimethylammonium

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bromide (CTAB) was prepared in doubly distilled water. All the chemicals and solvents used were of A.R. grade. Solutions for polarographic measurements were prepared by mixing 1.0 ml of the compound, 2.0 ml of methanol, 1.0 ml of 1.0 *M* KCl and 6.0 ml of the B.R. buffer. Polarograms were then recorded by adding CTAB 0.1 ml to 1.0 ml of each case. Dissolved oxygen was removed from the solution by passing purified hydrogen gas for about 10 min.

Apparatus: Polarographic curves were recorded on a Cambridge pen recording polarograph. The capillary characteristic was 2.07 $mg^{2/3} S^{1/2}$ at a zero potential in 1.0 *M* KCl solution. The temperature of the solution was maintained at 30 ± 0.1° by keeping the polarographic cell in a thermostatic bath. The *p*H metric measurements were made on the Expanded Scale L1 10 *p*H meter with glass electrodes SCE was used as the reference electrode.

Results and Discussion

All the compounds gave diffusion controlled, irreversible wave over the entire *p*H range (2.0-11.0) studied The half-wave potential was *p*H dependent whereas the limiting current was *p*H independent Afterwards, polarograms were recorded in presence of different amounts of CTAB (0.1-1.0 ml). In presence of surfactant also, diffusion controlled but more irreversible (Tables 1-5) waves were obtained $E_{\frac{1}{2}}$ of these waves were also *p*H dependent and the i_d remained *p*H independent.

TABLE 1 – VALUES OF $-\log K_{app}$ AND α_{app} FOR ELECTRO REDUCTION OF COUPLED PRODUCTS OF ARYLDIAZONIUM CHLORIDES WITH β-KETOESTER AT *p*H 6.0

R	$-\log K_{app}$ (cm⁻¹) (a)*	(b)*	α_{app} (a)*	(b)*
H	0.37	0.40	0.21	0.17
2-CH_3	0.30	0.35	0.25	0.22
3-CH_3	0.32	0.35	0.22	0.18
4-CH_3	0.37	0.41	0.22	0.19
2-Cl	0.25	0.32	0.21	0.16
3-Cl	0.32	0.35	0.27	0.21
4-Cl	0.32	0.36	0.22	0.18

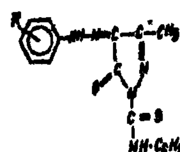
* (a) In the absence of surfactant.
(b) In the presence of surfactant.

TABLE 2—VALUES OF $-\log K_{app}$ AND α_{app} FOR ELECTRO REDUCTION OF 2-BENZOTHIAZOLYLHYDRAZONO ETHYL-2-CYANOETHANOATES AT *p*H 6.0

R	$-\log K_{app}$ (cm⁻¹) (a)*	(b)*	α_{app} (a)*	(b)*
H	0.28	0.30	0.14	0.10
2-CH_3	0.31	0.35	0.10	0.07
4-CH_3	0.27	0.31	0.12	0.08

* (a) In the absence of surfactant.
(b) In the presence of surfactant.

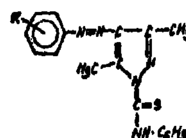
TABLE 3 – VALUES OF [illegible] K_{app} LOG AND α_{app} FOR ELECTRO REDUCTION OF 4-ARYLHYDRAZONO[illegible]-PHENYLTHIO CARBAMOYL-3-METHYL-2-PYRAZOLIN-5-ONES AT *p*H 6.0



R	$-\log K_{app}$ (cm⁻¹) (a)*	(b)*	α_{app} (a)*	(b)*
H	0.31	0.33	0.12	0.09
2-CH_3	0.39	0.40	0.10	0.06
2-OCH_3	0.36	0.41	0.14	0.11

* (a) In the absence of surfactant.
(b) In the presence of surfactant.

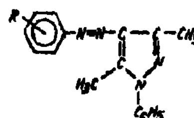
TABLE 4 – VALUES OF $-\log K_{app}$ AND α_{app} FOR ELECTRO REDUCTION OF N'-PHENYLTHIOCARBAMOYL-3,-5-DIMETHYL-4-ARYLAZOPYRAZOLES AT *p*H 6.0



R	$-\log K_{app}$ (cm⁻¹) (a)*	(b)*	α_{app} (a)*	(b)*
H	0.15	0.20	0.37	0.34
2-OCH_3	0.19	0.22	0.39	0.35
3-OCH_3	0.15	0.22	0.40	0.38

* (a) In the absence of surfactant
(b) In the presence of surfactant.

TABLE 5 – VALUES OF $-\log K_{app}$ AND α_{app} FOR ELECTRO REDUCTION OF N'-PHENYL-3,5-DIMETHYL-4-ARYLAZOPYRAZOLES AT *p*H 6.0



R	$-\log K_{app}$ (cm⁻¹) (a)*	(b)*	α_{app} (a)*	(b)*
H	0.23	0.28	0.32	0.30
2-CH_3	0.20	0.24	0.35	0.31
3-CH_3	0.21	0.24	0.32	0.28
4-CH_3	0.20	0.25	0.34	0.31
2-Cl	0.25	0.28	0.37	0.32
3-Cl	0.23	0.27	0.35	0.31
4-Cl	0.20	0.26	0.39	0.33

* (a) In the absence of surfactant
(b) In the presence of surfactant.

Rate of reduction (K_{app}) for both inner and outer sphere reduction at the mercury electrode surface is given by the equation,

$$\log K_{app} = \log \frac{i}{Fc_b}$$

where i is the current density at the rising part of the waves at a potential -E, c_b the bulk concentration of the depolarizer and K_{app} the rate constant

or reduction. In presence and absence of CTAB, values of K_{app} for all these compounds were calculated and are given in Tables 1-5. The above equation can be used successfully to differentiate between the two paths by monitoring the changes in the α_{app} in absence and presence of surfactants. If surfactant causes some change in the values of K_{app} it may be taken as a proof of inner sphere path otherwise it indicates outer sphere path.

It may be further observed that for a particular solution of constant concentration of the depolarizer and the supporting electrolyte, the plot of log K_{app} (determined at various potentials -E, on the rising part of the wave) against -E should be linear and is given by the equation :

$$\frac{\partial \log K_{app}}{\partial E} = \frac{\alpha I}{2.303\, RT}\left(\frac{\partial \Delta G^{0}_{AP}}{\partial E}+F\right) - \frac{1-\alpha_1}{2.303}\, RT\left(\frac{\partial \Delta G^{0}_{AR}}{\partial E}\right)$$

Since the magnitude and sign of the free energy terms will significantly vary for an inner - and outer-sphere path, the value of α_{app} will also vary. The α_{app} values thus can be utilised to differentiate between the two paths. The values of α_{app} has been evaluated from the slopes of plots (Tafel P lots) of log K_{app} against -E, which gives

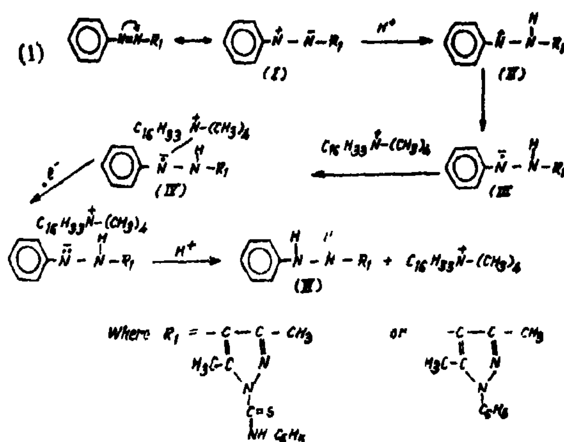
$$\alpha_{app} = -\frac{2.303\, RT}{1}\left(\frac{\partial \log K_{app}}{\partial E}\right)$$

when values of α_{app} are above 0.5, the electrode process is assumed to be taking in outer sphere whereas values lower than 0.5 indicates inner sphere path. Hence it is obvious that values of K_{app} and α_{app} for a particular compound may be utilised to distinguish between the inner and outer sphere path of the electrode reactions. α_{app} values for five series of compounds in presence and absence of surfactant are given in Tables 1-5.

On reviewing the data in Tables 1-5 some interesting trend in the values of K_{app} and α_{app} for these five series of compounds was observed. For azo compounds the values of K_{app} and α_{app} are higher than for hydrozono compounds. But for both type of compound viz., azo and hydrazono, K_{app} and α_{app} decreases in presence of surfactant indicating that reduction is taking place at the inner sphere of the electrode. Moreover, the values of α_{app} for azo and hydrazono compounds are below 0.5, and further point towards the inner sphere mechanism of the electrode process.

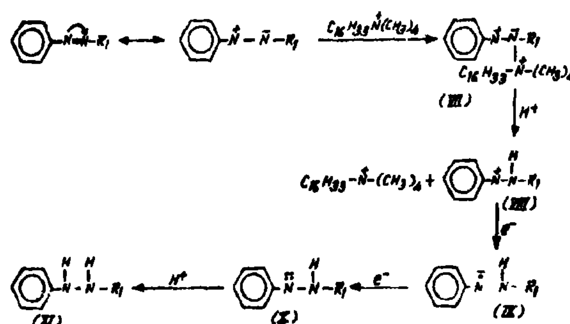
On the basis of values of K_{app} and α_{app} it appears possible to categorise azo and hydrazono compounds. Interestingly, compounds having azo group reduce at more positive potential ($E_{\frac{1}{2}}$=0.2 to 0.6, at pH 6.0) than compounds with hydrazono group ($E_{\frac{1}{2}}$=0.5 to 0.8 at pH 6.0), indicating the easy reduction of azo group to hydrazono group. Higher values of K_{app} and α_{app} in case of azo compounds are in similar tune.

The lower rate (K_{app}) of the electrode process in the presence of cationic surfactant (CTAB) may be due to the formation of surfactant depolarizer complex. The surfactant micelles do not diffuse as such in the outer plane of the Helmholtz double layer but it is the surfactant depolarizer complex which reaches the inner part of the double layer, orients itself towards electrode surface and subsequently get reduced. The possible mechanism may be as follows (H^+, e, e, H^+ mechanism)[18] :



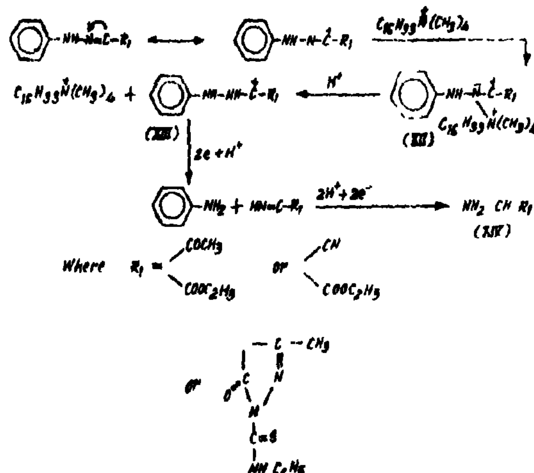
In this mechanism free radical (III) form surfactant-depolarizer complex with cationic surfactant (CTAB). This surfactant-depolarizer complex may diffuse to the inner part of the double layer and get reduced to (VI) after the uptake of an electron and a proton, and releasing the surfactant as such.

(2) Alternatively,



This mechanism appears to be more probable due to the easy availability of species C_6H_5-$\overset{+}{N}$-$\overset{-}{N}$-R in the solution. After the formation of phenylazo-functionalised surfactant (VII) (formed by the interaction of polarizer -N=N- group) it gets protonated to give protonated species (VIII). The protonated intermediate then reduces to (XI) similarly as in the case of mechanism (1).

In the same way, effect of cationic surfactant on hydrazono compounds can be explained on the basis of more probable mechanism (2), as follows :



Here, functionalised surfactant (XII) which reaches the inner part of the double layer, get reduced to give aniline and another amine (XIV), following the steps (H^+, e^-, e^-, H^+).

It is quite clear from the above mechanism that reduction of hydrazono group involves initial breakage of -NH-N- bond followed by uptake of two more protons and electrons. Since more energy is required for the cleavage of-NH-N- bond, $E_{\frac{1}{2}}$ is more negative than azo compounds.

Acknowledgement

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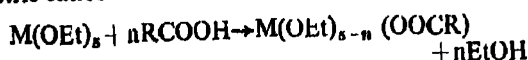
Benzilic Acid Complexes of Niobium(V) and Tantalum(V)

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Reactions of pentaethoxides and pentachlorides of niobium and tantalum with benzilic acid have been carried out in different molar ratios and compounds of the type, $[M(OEt)_{5-2n}(Bz)_n]$ and $[MCl_{5-2n}(Bz)_n]$ (where Bz represents the benzilato group, M=Nb or Ta and n=1 or 2) have been isolated Alcoholysis reactions of $[M(OEt)_{5-2n}(Bz)_n]$ with excess of *tert*-butanol were also carried out and product of type, $[M(OBu^t)_{5-2n}(Bz)_n]$ were obtained All the new complexes synthesised were characterised by elemental analysis, molecular weight determinations, ir and nmr spectral studies.

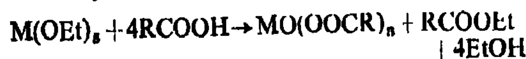
IN earlier publication, we have reported the synthesis of some novel β-diketonates[1] of niobium and tantalum Now, we report the synthesis of some benzilates of niobium and tantalum(V). Funk and coworkers[2] have reported that basic acetates are formed by the reaction of pentachlorides of niobium and tantalum with acetic acid Pentaethoxides of niobium and tantalum react with lower and higher carboxylic acids in different stoichiometric ratios[3].



$$M(OEt)_5 + nRCOOH \rightarrow M(OEt)_{5-n}(OOCR) + nEtOH$$

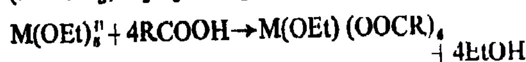
(where M=Nb or Ta and n=1, 2 or 3)

However, when the reactions were carried out in molar ratio 1 : 4 or 1 : >4 the lower carboxylic acids gave the corresponding basic carboxylates and the higher carboxylic acids formed monoethoxide tetracarboxylates.



$$M(OEt)_5 + 4RCOOH \rightarrow MO(OOCR)_3 + RCOOEt + 4EtOH$$

$(R=CH_3, C_2H_5 \text{ or } C_3H_7)$

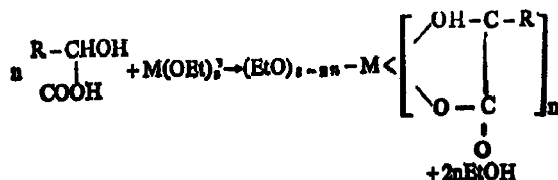


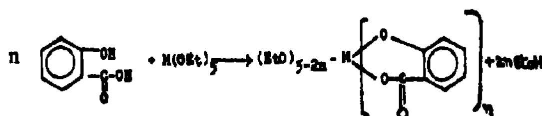
$$M(OEt)_5 + 4RCOOH \rightarrow M(OEt)(OOCR)_4 + 4EtOH$$

$(R=C_{11}H_{23}, C_{15}H_{31} \text{ or } C_{17}H_{35})$

These derivatives are soluble in common organic solvents except the basic carboxylates which are insoluble.

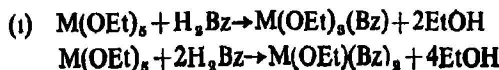
Kapoor and coworkers[4] have reported the reactions of pentaethoxides of niobium and tantalum with various hydroxy carboxylic acids e g., lactic, mandelic or salicylic acids :



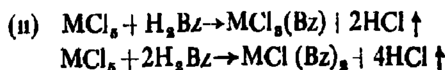


Recently we have studied the reactions of isopropoxides and chlorides of aluminium, titanium, and zirconium with benzilic acid and interesting results were obtained[5]. A survey of literature reveals that no such work has been done with niobium and tantalum.

In view of the above, it was considered worthwhile to study the reactions of ethoxides and chlorides of niobium and tantalum with benzilic acid in different molar ratios in refluxing benzene :



(i) $M(OEt)_5 + H_2Bz \rightarrow M(OEt)_3(Bz) + 2EtOH$
$M(OEt)_5 + 2H_2Bz \rightarrow M(OEt)(Bz)_2 + 4EtOH$



(ii) $MCl_5 + H_2Bz \rightarrow MCl_3(Bz) + 2HCl\uparrow$
$MCl_5 + 2H_2Bz \rightarrow MCl(Bz)_2 + 4HCl\uparrow$

(where M=Nb or Ta, H_2Bz=Benzilic acid)

The completion of reaction was checked by estimating the liberated ethanol azeotropically[6] in case of ethoxides and HCl(gas) in case of chloride reactions.

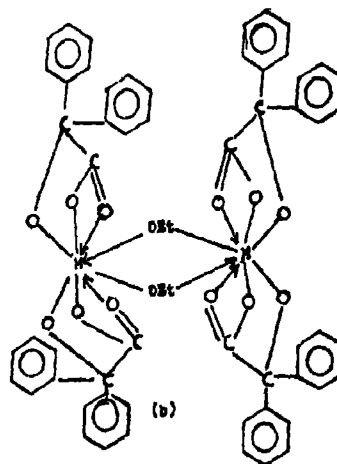
In both the reactions, it was found that reaction proceeds with the removal of only four moles of ethanol or chlorine even when excess of benzilic acid was used. It has been observed that removal of the fifth mole of ethoxy as well as chloride is very difficult even when an excess of the ligand was taken and refluxing time was increased. This may be attributed to steric hindrance of the bulky benzilic acid or saturated coordination state of metal in disubstituted derivatives.

The complexes isolated are highly soluble in organic solvents in the case of ethoxide derivatives

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while the chloride derivatives are partially soluble in $CHCl_3$, CCl_4 and benzene. These chloro complexes are soluble in dimethyl formamide and dimethyl sulphoxide. Attempts were also made to sublime them under reduced pressure, but they tend to decompose at ~ 120-160°/0.02 mm.

The nmr spectra of the compounds (Table 1) $[M(OEt)_{5-2n}(Bz)_n]$ (where M=Nb or Ta and n=1 or 2) in $CDCl_3$ show CH_3 protons and $-CH_2$ protons of ethoxy group in the region 1.1-1.3 ppm as triplet and 3.5-3.9 ppm as quadruplet respectively[7] (Table 1). The multiplet in the region 6.9-7.2 ppm clearly indicate the presence of phenyl ring[7]. The chloro substituted benzilato derivatives show a multiplet in the region 7.1-7.4 ppm which may be assigned to the protons of phenyl group.



The infrared spectra of mono and *bis* benzilato derivatives of Nb(V) and Ta(V) show no absorption band in the ~3400 cm^{-1} region indicating the absence of hydroxy groups (alcoholic as well as carboxylic) of benzilic acid.

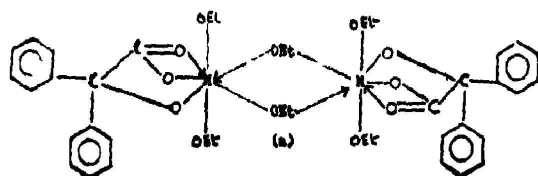
TABLE 1—CHARACTERISTICS INFRARED AND NMR DATA FOR BENZILATE COMPLEXES OF NIOBIUM AND TANTALUM

Sl No.	Complex	$\nu_{(C=O)}$ cm^{-1} (ir data)	$\nu_{(M-O)}$ cm^{-1} (ir data)	$-CH_3$ of ethoxy (nmr data)	$-CH_2$ of ethoxy (ppm) in δ	–phenyl ring
1.	$[Nb(OEt)_3(Bz)]$	1630 s	550 s	1.1–1.3 (t)	3.5–3.7 (q)	7.0–7.2 (m)
2.	$[Nb(OEt)(Bz)_2]$	1630 s	560 s	1.2–1.4 (t)	3.5–3.7 (q)	7.0–7.2 (m)
3.	$[Ta(OEt)_3(Bz)]$	1625 s	535 sb	1.1–1.3 (t)	3.4–3.7 (q)	7.1–7.4 (m)
4	$[Ta(OEt)(Bz)_2]$	1640 sb	555 sb	1.1–1.3 (t)	3.3–3.5 (q)	7.2–7.4 (m)
5	$[NbCl_3(Bz)]$	1660 s	550 m	–	–	6.9–7.2 (m)
6.	$[NbCl(Bz)_2]$	1610 s	550 m	–	–	6.9–7.1 (m)
7	$[TaCl_3(Bz)]$	1680 s	550 mb	–	–	7.0–7.2 (m)
8.	$[TaCl(Bz)_2]$	1670 s	550 mb	–	–	6.9–7.3 (m)

The asymmetric carbonyl stretching frequency which appeared at 1740 cm^{-1} as a strong band in benzilic acid has been shifted to lower frequency (60–80 cm^{-1}) indicating the coordination of >C=O group to the metal. The strong band at ~535–560cm^{-1} may be assigned to $\nu(M-O)$ while $\nu(M-Cl)$ absorbed at ~390 cm^{-1}. The other characteristic bands are assigned in Table 3.

The molecular weight of soluble complexes in refluxing benzene were determined and found that these complexes are of dimeric nature.

On the basis of above studies and elemental analysis, the following seven and eight coordinated structures can tentatively be assigned to compounds of the type $[M(OEt)_{5-2n}(Bz)_n]$ (where M=Nb or Ta and n=1 or 2) respectively.



It appears that in *bis* derivatives of niobium or tantalum, the metal atoms are so well shielded in dimeric structure that further coordination of reacting benzilic acid molecule becomes sterically hindered. Due to this, further reaction do not take place even with excess of ligand with prolonged refluxing.

Due to partially soluble nature of chloro complexes in benzene it was not possible to determine their molecular weight.

Alcoholysis reactions of the compounds $[M(OEt)_{5-2n}(Bz)_n]$ were also carried out with excess of *tert*-butanol and compounds having general formula, $[M(OBu^t)_{5-2n}(Bz)_n]$ where M=Nb or Ta, and n=1 or 2, were isolated and characterised (Table 2). The liberated ethanol was estimated by oxidimetric method[6].

Experimental

All glass apparatus with standard quickfit joints were used throughout the experimental work. Stringent precautions were taken to exclude moisture.

Benzene (AR,BDH), ethanol, *tert*-butanol (SD) were dried and purified by standard methods. $NbCl_5$(Fluka), $TaCl_5$ (Riedel), benzilic acid AnalaR

TABLE 2—INTERCHANGE REACTIONS OF $[M(OEt)_{5-2n}(L)_n]$ WITH *tert*-BUTANOL
(where M = Nb or Ta and n = 1 or 2, L = Benzilic acid)

Sl. No.	Reactants: Complex taken (g) (mole)	Reactants: Wt. of *tert*-butanol taken (g)	Refluxing time (hr)	Product formed, state and decomposition temp	Analysis: Metal (%) Found (Calcd)	Analysis: Amount of ethanol in azeotrope (g) Found (Calcd)
1.	$Nb(OEt)_3(Bz)$ 0.19 (0.0004)	excess	7	$[Nb(OBu^t)_3(Bz)]$ Light yellow, solid 165	17 9 (17 2)	0 06 (0 06)
2.	$Nb(OEt)(Bz)_2$ 0.40 (0.0007)	excess	6	$[Nb(OBu^t)(Bz)_2]$ Light yellow, solid 150	16 0 (15 9)	0 03 (0 03)
3.	$Ta(OEt)_3(Bz)$ 0.39 (0.0007)	excess	8	$[Ta(OBu^t)_3(Bz)]$ Light yellow, solid 210	28 3 (28 9)	0 10 (0 10)
4.	$Ta(OEt)(Bz)_2$ 0.56 (0.0008)	excess	6	$[Ta(OBu^t)(Bz)_2]$ Light yellow, solid 180	25 4 (25 6)	0 04 (0 04)

grade (E. Merck) were used as supplied Niobium and tantalum pentaethoxides were prepared by standard methods[8,9,10].

Molecular weights were determined in benzene with the help of semimicro ebulliometer (Gallenkamp) using thermistor sensing. The ir spectra were recorded on a Perking Elmer-621 spectrophotometer using nujol mulls, cesium iodide pellets or KBr pellets. The nmr spectra were recorded in $CDCl_3$ on Perkin Elmer R-32 spectrometer Ethanol was estimated by oxidimetric method[6] using $N\ K_2Cr_2O_7$ in 12.5% sulphuric acid. Niobium and tantalum were estimated as Nb_2O_5 and Ta_2O_5 by direct ignition of compounds after digestion with ammonia and nitric acid in platinum crucible. C, H were determined by micro analytical laboratory of Chemistry Department, Delhi University, Delhi

Reactions :

(i) *Reaction of niobium pentaethoxide and benzilic acid (molar ratio 1 : 1)* : To a solution of $Nb(OEt)_5$ (0.46 g, 0.0014 *M*) in benzene was added benzilic acid (0 33 g ; 0 0014*M*) A suspension appeared at the time of addition which became clear after refluxing for 6 hr The ethanol liberated during the reaction was collected azeotropically and estimated[6]. The excess of solvent was distilled off and final product was dried under vacuum at 40°/0 5 mm, a light yellow solid was obtained.

Found : Ethanol in azeotrope 0 13 g ; Nb, 20.46 %. Calcd for $[Nb(OEt)_3(Bz)]$: ethanol in azeotrope, 0.13 g ; Nb, 20.7 %.

For the sake of brevity other reactions are given in Table 3a.

TABLE 3a—REACTIONS OF NIOBIUM AND TANTALUM PENTA ETHOXIDES WITH BENZILIC ACID

Sl. No	Molar ratio	Alkoxide g (mole)	Benzilic acid g (mole)	Refluxing time (hr)	Product, state, yield (%) and decomposition temp (°C)	Amount of alcohol in azeotrope (g). Found (Calcd)	Analysis: Metal % Found (Calcd)	Analysis: C % Found (Calcd)	Analysis: H % Found (Calcd)	Mol wt in benzene : Found (Calcd)
1.	1 : 1	0 46 (0 0014)	0.33 (0.0014)	6	$[Nb(OEt)_3(Bz)]$ Light yellow, solid (80) 180	0 13 (0 13)	20 7 (20 4)	52 5 (53 0)	4 2 (5 5)	895 3 (454 3)
2.	1 : 2	0 44 (0 0013)	0 63 (0.0027)	8	$[Nb(OEt)(Bz)_2]$ Light yellow, solid (80) 173	0 23 (0 25)	16 2 (15 7)	-	-	1200 0 (590 4)
3.	1 : 1	0.93 (0.0023)	0 52 (0 0023)	7	$[Ta(OEt)_3(Bz)]$ Light yellow, solid (85) 192	0 21 (0 21)	33 4 (33 3)	45 7 (44 4)	3 9 (4 4)	1096.8 (542 3)
4.	1 : 2	0.76 (0.0018)	0 85 (0.0037)	10	$[Ta(OEt)(Bz)_2]$ Light yellow, solid (88) 199	0 35 (0.35)	26 5 (26 7)	51 9 (53 2)	2 9 (3 7)	1219 0 (678 4)

TABLE 3(b) – REACTIONS OF NIOBIUM AND TANTALUM PENTA CHLORIDES WITH BENZILIC ACID

Sl. No.	Molar ratio	Metal chloride g (mole)	Benzilic acid (g) (mole)	Refluxing time (hr)	Product, state yield (%) and decomposition temp (°C)	Metal (%) Found (Calcd)	Chlorine(%) Found (Calcd.)	C (%) Found (Calcd.)	H (%) Found (Calcd)
1.	1 : 1	1 82 (0.0067)	1 54 (0 0067)	36	$[NbCl_3(Bz)]$ Light brown, solid (80) 195	22 1 (21.8)	24.5 (24 9)	39 2 (39 6)	2 5 (2.4)
2.	1 · 2	1 03 (0.0038)	1 75 (0 0076)	50	$[NbCl(Bz)_2]$ Light brown, solid (78) 190	16 4 (15 9)	6 0 (6 1)	56.1 (58.0)	4.6 (3 5)
3.	1 · 1	1 01 (0 0028)	0 64 0 0028)	40	$[TaCl_3(Bz)]$ Light brown, solid (80) 140	35 0 (35 2)	20 5 (20.7)	31 4 (32 8)	2 4 (1 9)
4	1 · 2	0 87 (0 0024)	1 10 (0 0048)	60	$[TaCl(Bz)_2]$ Light brown, solid (80) 140	26 8 (27 0)	5 6 (5 2)		

(ii) *Reaction between* tris *ethoxy niobium(V) benzilate and excess of* tert-*butanol* To a solution of $[Nb(OEt)_3(Bz)]$ (0.19 g ; 0 0004 *M*) in benzene was added excess of *tert*-butanol (~5 ml) and the mixture was refluxed for 7 hr The ethanol so liberated was collected azeotropically and estimated[6] The excess of solvent was distilled off and the final product was dried under *vacuo* at 40°/0 5 mm , a light yellow solid was obtained

Found : Ethanol in azeotrope, 0 05 g, Nb, 18 2 % Calcd. for $[Nb(OBu^t)_3(Bz)]$; ethanol in azeotrope 0.05 g ; Nb, 17.9 %.

The details of other reactions are given in Table 2

(iii) *Reaction between niobium pentachloride and benzilic acid(H_2Bz) (molar ratio 1:1)* : Benzilic acid (1.54 g ; 0.0067*M*) was added to a suspension of niobium pentachloride (1.82 g ; 0 0067*M*) in benzene An exothermic reaction started with evolution of hydrogen chloride gas The mixture was refluxed in an oil bath at 110° for about 36 hr and checked continuously. When no more hydrogen chloride gas evolved, the reaction mixture was cooled to room temperature and excess of solvent was removed under reduced pressure leaving behind a light brown solid mass.

Found : Nb, 21 8 % ; Cl, 24 5 % Calcd. for $NbCl_3(Bz)$; Nb, 22 1 · Cl, 24 9 %.

The other reactions are given in Table 3b

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Structural Studies of Cu(II) and Ni(II) Complexes with Physiologically Active Ligands

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Cu(II) and Ni(II) complexes of physiologically active coumarin derivative, 8-acetyl-4-methyl umbelliferone and its oxime, hydrazone and thiosemicarbazone derivatives have been synthesized in the pH range of 5 5-8 00 These complexes have been characterized by elemental analysis, conductivity, ir and electronic spectra, magnetic moments and TGA. Cu(II) and Ni(II) complexes of 8-acetyl-4-methyl umbelliferone and its thiosemicarbazone have been found to possess polymeric structures with the oxygen of the lactone carbonyl participating in coordination, resulting in octahedral and square planar dispositions respectively Physiological activities of ligands and their metal chelates have been evaluated by kymographic studies

IOUMARIN (2H-1-benzopyran-2-one) and its derivatives have been found to exhibit physiological activity and are also extensively used as alytical reagents[1-3]. Metal complexes of coumarin rivatives with hydroxy, acetyl and phenyl azo bstituents as coordinating centres have been dely studied[4-6]. Umbelliferone (7-hydroxy umarin) known for its antibiotic, antifungal activi-s[7,8] having substituents like amino and nitro at sition-8 and methyl at position-4 has been investi-ted for complexing ability[9,10] 8-Acetyl-4-methyl nbelliferone has been found to exhibit anticoagunt and plant growth regulant property[11,12]. In is communication we are reporting the synthesis id structural studies of Cu(II) and Ni(II) comexes of 8-acetyl-4-methyl umbelliferone (AMU) id its oxime (AMUO), hydrazone (AMUH) and iosemicarbazone (AMUT) derivatives (Figs. 1-4). metal complexes of AMU, AMUO and AMUH is also being reported.

Experimental

Methods and materials : All the solvents and reagents used were of AnalaR grade Magnetic susceptibility was obtained at room temperature by using Faraday technique. Infrared spectra (4000-200 cm^{-1}) were recorded on a high resolution Perkin-Elmer-577 IR spectrophotometer in KBr pellets Electronic (mull) spectra were recorded on a Varian Cary-17D instrument (200-700 nm) Conductance measurements were done on a Philips conductivity bridge (model No. 3201). Carbon, hydrogen and nitrogen contents in the ligand and the complexes were estimated by microanalysis. The metal estimations were carried out following standard

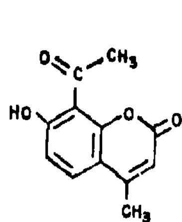


Fig 1
AMU

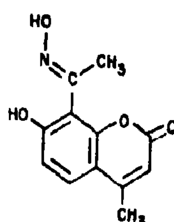


Fig 2
AMUO

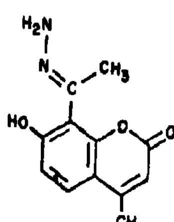


Fig 3
AMUH

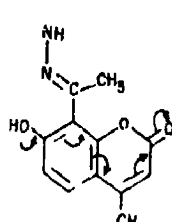


Fig 3i
AMUH

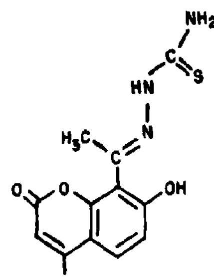


Fig 4
AMUT

is interesting to note that in the complexes of MU and AMUT, the oxygen of lactone carbonyl articipates in coordination resulting in polymeric ructures. Our observation regarding the behaviour f AMU with Cu(II) is entirely different from the ported one[13]. The kymographic study[14] of the procedures[15]. Thermogravimetric analyses were carried out in a manually operated thermo-balance.

Synthesis : 8-Acetyl-4-methyl umbelliferone has been prepared by earlier reported procedure[16,17]. The Schiff bases of AMU have been obtained by the standard procedures[18].

'For correspondence.

A hot solution of metal chloride (0.01 mole) in methanol (50 ml) was added to the hot solution of the respective ligand (0.03 mole) in methanol (100 ml). The reactants were refluxed on steam bath for about 2 hr. The complexes separated out after adjusting the *p*H in the range of 5.5-8.00. The resulting products were filtered in hot condition, washed with methanol, petroleum ether and dried in vacuum.

Results and Discussion

All the complexes are stable to air and moisture They decompose at higher temperatures. The complexes are insoluble in water and common organic solvents. Some of them are soluble sparingly in DMF, DMSO. The negligibly low values of molar conductance around 5-6 ohm^{-1} cm^2 $mole^{-1}$ of these complexes in 1×10^{-3} *M* DMF solution suggest their non-electrolytic behaviour. Elemental analysis (Table 1) indicates metal to ligand ratio as 1 : 2 for Cu(II) and Ni(II) complexes of AMU, AMUH and AMUO and 1 : 1 in AMUT chelates IR spectral data of the ligands and metal complexes are given in Table 2. The magnetic and electronic spectral data are included in Table 3.

TABLE 1—ANALYTICAL DATA : CALCD (FOUND) %

Compound	C	H	N	S	Metal
AMU($C_{11}O_4H_{10}$)	66 05 (65.5)	4 58 (4.5)	–	–	–
Cu($C_{11}O_4H_9$)$_2$	57.88 (47·80)	4.02 (4.1)	–	–	12.77 (12.70)
Ni($C_{11}O_4H_9$)$_2$	58.45 (58 51)	4 06 (4 1)	–	–	11 92 (11.89)
AMUH($C_{12}O_3N_2H_{12}$)	62 06 (62 0)	5 17 (5 11)	12 06 (12.2)	–	–
Cu($C_{12}O_3N_2H_{11}$)$_2$	54.80 (54 7)	4 18 (4 1)	10.65 (10 55)	–	12 09 (11.92)
Ni($C_{12}O_3N_2H_{11}$)$_2$ 2H_2O	51 73 (51.56)	4 67 (4.61)	10 06 (10 1)	–	10 54 (10 2)
AMUO($C_{12}O_4NH_{11}$)	61 80 (61.59)	4 29 (4.32)	6 01 (5 98)	–	–
Cu($C_{12}O_4NH_{10}$)$_2$	54.59 (54 62)	3 79 (3 72)	5 31 (5 25)	–	12 04 (12 12)
Ni($C_{12}O_4NH_{10}$)$_2$ 2H_2O	51 54 (51.0)	4 29 (4 3)	5 01 (5 0)	–	10 51 (10 2)
AMUT($C_{12}O_3N_3SH_{13}$)	53 60 (53 1)	4 57 (4.6)	14 43 (14 40)	–	–
Cu($C_{12}O_3N_3SH_{11}$)	44 25 (44 1)	3 12 (3 10)	11 91 (11 79)	9 07 (8 98)	18 02 (17 92)
Ni($C_{11}O_3N_3S_{11}$)	44 85 (44 4)	3 16 (3 21)	12 18 (12.20)	9 20 (9.18)	16 88 (16 5)

TABLE 3—MAGNETIC AND ELECTRONIC SPECTRAL DATA

Complex	Electronic spectra (cm^{-1})	Magnetic data (B M.) μ_{eff}
Cu(II)AMU	13000–16000, 28600	2 00
Ni(II)AMU	15380, 20400, 23280, 28315	2.98
Cu(II)AMUT	16300, 18000, 20000	1.9
Ni(II)AMUT	20000	Diamagnetic
Cu(II)AMUH	16100, 18500, 20000	1 99
Ni(II)AMUH	16160, 20000, 21740	2.99
Cu(II)AMUO	18000–21000	1 8
Ni(II)AMUO	16666, 21280, 22220, 25000	3.1

Complexes of AMU: The ir spectrum of the ligand AMU does not show any band characteristic of hydroxyl group in 3600-2500 cm^{-1} region, which is in accordance with the observation made by Sabata and Rout[19]. The absence of this band is attributed to strong intramolecular hydrogen bonding between 7-hydroxy and 8-acetyl group. A strong band observed at 1740 cm^{-1} has been assigned to ν(C=O)[20] (lactone) and two bands at 1625 and 1205 cm^{-1} to hydrogen bonded ν(C=O) acetyl and ν(C–O) phenolic respectively. A medium band at 1060 cm^{-1} is characterized for ν_{asy}(C-O-C)[21] corresponding to the cyclic ether grouping. In comparison with the ligand spectrum, the spectra of Cu(II) and Ni(II) complexes have shown downward shifts (35-40 cm^{-1}) in the ν(C=O) acetyl and upward shift (15-20 cm^{-1}) in the ν(C–O) phenolic groups indicating coordination through the acetyl oxygen and deprotonated phenolic oxygen respectively. An interesting feature observed is the red shift in ν(C=O) lactone to the extent of about 25 cm^{-1}, suggesting coordination through the lactone oxygen. This is further supported by downward shift in ν_{asy}(C-O-C) of the pyran ring On the basis of ir data it is concluded that AMU behaves as a monobasic ligand coordinating not only through phenolic and acetyl oxygen but also through lactone oxygen New bands in the region of 370-460 and 360-480 cm^{-1} in both the complexes are assignable to stretching frequencies of (M –O) and (M - N) bonds respectively[22].

TABLE 2—IR SPECTRAL CHARACTERISTICS OF LIGANDS AND THE METAL COMPLEXES (cm^{-1})

Compound	νOH	νNH_2 asy	νNH_2 sy	ν(C=O) (lac)	ν(C=O) (ace)	ν(C=N)	ν(C–O)
AMU	–	–	–	1740(s)	1625(s)	–	1205(s)
Cu(II)AMU	–	–	–	1715(s)	1585(s)	–	1225(s)
Ni(II)AMU	–	–	–	1720(s)	1590(s)	–	1220(s)
AMUT	3350(m)	3250(s)	3150(s)	1720(s)	–	1600(s)	1220(s)
Cu(II)AMUT	–	3250(s)	3150(s)	1700(s)	–	1575(s) & 1610(s)	1240(s)
Ni(II)AMUT	–	3250(s)	3150(s)	1705(s)	–	1580(s) & 1610(s)	1240(s)
AMUH	3220(m)	3350(s)	3250(s)	1700(s)	–	1600(s)	1230(s)
Cu(II)AMUH	–	3350(s)	3250(s)	1720(s)	–	1575(s)	1240(s)
Ni(II)AMUH	–	3350(s)	3250(s)	1720(s)	–	1580(s)	1240(s)
AMUO	3300–3200(s,b)	–	–	1720( )	–	1600(s)	1230(s)
Cu(II)AMUO	3200(s)	–	–	1720(s)	–	1580(s)	1240(s)
Ni(II)AMUO	3100–3600(s,b)	–	–	1720(s)	–	1585(s)	1235(s)

s = strong, m = medium; b = broad.

The magnetic moments for Cu(II) and Ni(II) AMU complexes were found to be 2.00 and 2.98 B.M. respectively at room temperature, showing the presence of one and two unpaired electrons. The electronic spectrum of Cu(II) complex shows a broad band in the region of 13000-16000 cm^{-1} and intense band at 28600 cm^{-1}. The first band can be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition, suggesting octahedral geometry[23] and the remaining band to charge transfer. Four electronic spectral bands have been observed at 28315, 23250, 20400 and 15380 cm^{-1} for Ni(II) complex. The first one being intense is attributed to charge transfer. The 15380 and 23250 cm^{-1} bands are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions[24]. The weak band observed at 20400 cm^{-1} is attributed to spin-forbidden transition between the triplet and singlet transition i.e., $^3A_{2g} \rightarrow {}^1T_{1g}$[25]. These transitions are in accordance with octahedral geometry. In view of the insoluble nature and lactone carbonyl participation in coordination, polymeric structures with octahedral geometry have been proposed (Fig. 5).

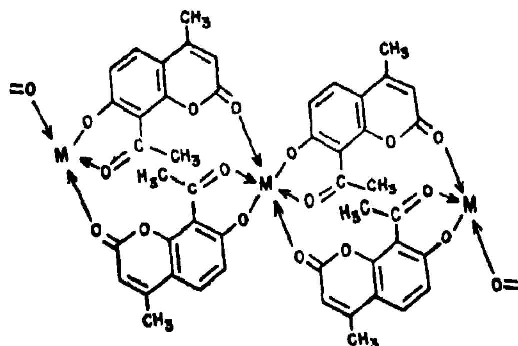


Fig 5 AMU complexes, M = Cu(II) or Ni(II).

Complexes of AMUT : The ir spectrum of the ligand shows bands at 3350, 3250 and 3150 cm^{-1} which are assignable to ν(OH) chelated, ν_{asy} NH_2 and ν_{sy} NH_2 respectively. The bands at 1720 and 1600 cm^{-1} are characterized for ν(C=O) lactone and ν(C=N). A medium band at 1170 cm^{-1} is attributed to ν(C=S)[26]. The disappearance of the band due to ν(OH) in complexes suggest deprotonation of phenolic group and subsequent bonding through this oxygen. There is a red shift in ν(C=O) lactone by about 20 cm^{-1} in both the complexes indicating the participation of oxygen of lactone carbonyl in chelation. Another feature observed is the absence of the band due to ν(C=S) and appearance of a new band at 1610 cm^{-1} characteristic of ν(C=N). This indicates the conversion of the ligand from thione to thiol form during complex formation[27]. The ν(S-H), which generally appears in 2590-2450 cm^{-1} region[28] is absent in the complexes indicating deprotonation of -SH group and subsequent coordination through sulphur. In the spectrum of the complexes, a red shift is observed in the original ν(C=N). This is attributed to the binding of nitrogen of the original azomethine group. Thus it is concluded that ligand (AMUT) acts as dibasic tridentate.

Magnetic moment data show that Cu(II) complex is paramagnetic (μ_{eff}=1.9 B.M.) whereas Ni(II) complex is diamagnetic. Three electronic spectral bands at 20000, 18000, 16300 cm^{-1} are assignable to $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively[29], suggesting square planar geometry for Cu(II) complex. Diamagnetic nature of Ni(II) complex is consistent with square planar arrangement[30] (Fig 6). It is further supported by an electronic spectral band at 20000 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition[31].

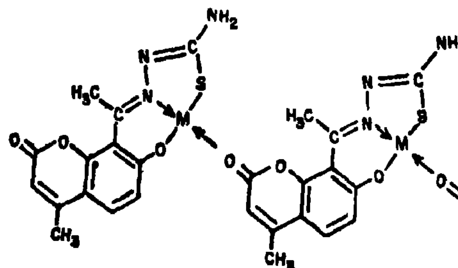


Fig. 6. AMUT complexes, M = Cu(II) or Ni(II).

Complexes of AMUH ; The ir spectra of the ligand show bands at 3350, 3250 and 3220 cm^{-1} assignable to $\nu_{asy}NH_2$, $\nu_{sy}NH_2$ and νOH chelated. The bands at 1700, 1600 and 1230 cm^{-1} are due to ν(C=O) lactone, ν(C=N) and ν(C-O) phenolic respectively. In metal chelates, the disappearance of the band due to ν(OH) and blue shift in ν(C-O) confirm the deprotonation of phenolic -OH group and complexation through oxygen. There is no change in the νNH_2 bands indicating its non-involvement in coordination. The bathochromic shift in ν(C=N) (20 cm^{-1}) indicates coordination through azomethine nitrogen. In contrast to AMU complexes a hypsochromic shift has been observed in ν(C=O) lactone. The probable explanation in this case may be that the resonance participation of the electron pair on oxygen reported in similar compounds[32](Fig. 3a) is diminished by the substitution of metal ion in place of hydrogen atom which will result in increasing double bond character between lactone oxygen and carbon and hence the hypsochromic shift and the non-participation of oxygen of lactone carbonyl in coordination. A broad trough in the region of 3380-3450 cm^{-1} and a medium band at 850 cm^{-1} suggests the presence of coordinated water in Ni(II) complex[33]. Thermogravimetric analysis reveals weight loss equivalent to two water molecules per mole of the Ni(II) complex at~140°. A few weak absorptions observed at 490 and 520 cm^{-1}, 485 and 520 cm^{-1} for Cu(II) and Ni(II) complex are attributed to ν(M-N) and and ν(M-O)[22].

The observed magnetic moment value for the Cu(II) complex is 1.99 B.M. The electronic spectrum shows three bands at 16100, 18500 and 20000 cm^{-1} which can be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions[29] respectively indicating square planar geometry. (Fig 7).

The Ni(II) complex shows magnetic moment value of 2 9 B.M which is in the range expected for octahedral complexes The electronic spectrum shows three bands at 16160, 20000 and 21740 cm^{-1} The first two are assigned to $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ transition[24]. The last weak band observed at 20000 cm^{-1} is assignable to spin-forbidden $^3A_{2g} \rightarrow ^1T_{1g}$ transition[25]. On the basis of above observations Ni(II) complex is assigned octahedral geometry (Fig. 8)

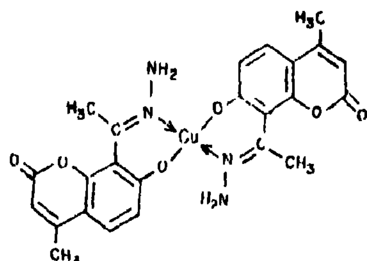


Fig. 7 AMUH complexes

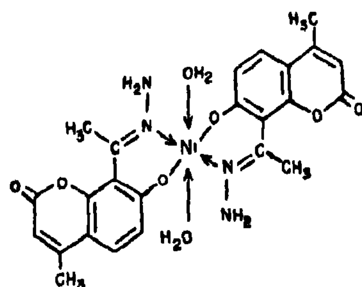


Fig 8 AMUH complexes

Complexes of AMUO The broad bands at 3300-3200 cm^{-1} and the strong bands at 1700, 1600, 1230 cm^{-1} in the ir spectrum of the ligand are assigned to hydrogen bonded -OH stretchings of phenol and oxime groups, ν(C - O) lactone, ν(C -N), ν(C O) phenolic respectively Cu(II) complex shows a strong band at 3200 cm^{-1} assignable to ν(-OH) oxime, involved in intramolecular hydrogen bonding[14] A broad trough in case of Ni(II) complex in the region of 3100-3400 cm^{-1} is attributed to the presence of coordinated water which is supported by a band of medium intensity around 940 cm^{-1} [21] Thermogravimetric analysis confirms the presence of two water molecules per mole of Ni(II) complex In both the complexes there is a downward shift of ν(C N) (15-20 cm^{-1}) indicating participation of azomethine nitrogen in bonding An upward shift observed in case of ν(C-O) phenolic suggest coordination through this oxygen. The blue shift in ν(C=O) lactone in both the complexes can be explained on the same line as described earlier in AMUH complexes.

The observed magnetic moments are 1.8 B.M. and 3.1 B.M for Cu(II) and Ni(II) complexes respectively. The electronic spectral bands in the range of 18000-21000 cm^{-1} in Cu(II) complex and 16000-25000 cm^{-1} in Ni(II) complex are indicative of square planar and octahedral geometries respectively (Figs. 9 and 10)

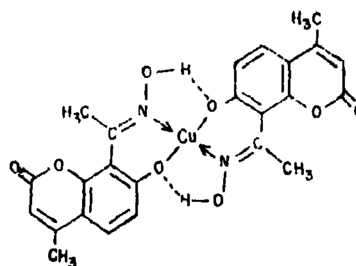


Fig 9 AMUO complexes

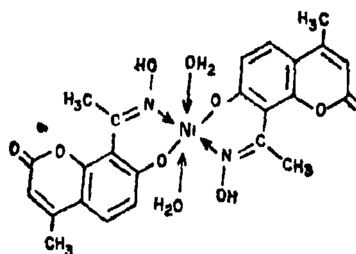


Fig. 10. AMUO complexes.

Physiological study : Frog's heart was isolated by opening the thoracic cavity from a doubly pithed frog Ringer solution which is isoosmotic and isotonic was used for profusion studies in the isolated heart Glucose was added to the ringer as an energy supplement Heart beat and the rhythm were recorded on a smoked cylinder attached to kymograph drum moving at a slow speed (1 5 rpm), following the reported procedure[14] Aqueous solutions of the metal chlorides and the ligands of 10 ppm concentration at pH 7 4 were used to study the effects on the isolated heart. The ligand solutions followed by solution mixtures

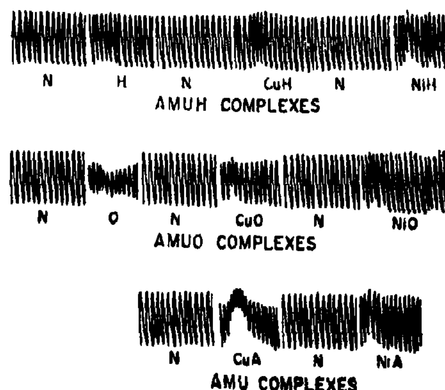


Fig. 11. N = Normal, H = AMUH, O = AMUO, A = AMU Kymograms

containing the metal and ligand in appropriate proportions for complex formation, were introduced into the heart, along with the profusion fluid At the end of each test the heart was allowed to return to normal speed and rhythm by allowing pure ringer solution to profuse through the heart The time taken by the heart to return to the normal rhythm and speed however varied from ligand to ligand and also from complex to complex. In general the Cu(II) complexes did not exert changes in the systolic beat while Ni(II) complexes appeared to have altered the systolic beat more than the diastolic beat. Ligands in general accelerated speed while their complexes increased the rhythm further. The relevant kymograms are given in Fig. 11. This type of work was reported in case of some substituted coumarins on profused rabbit heart[35]. Studies are in progress regarding the anticoagulant properties of these complexes.

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MNDO Study of Reaction Paths : Hydroboration of Organic Nitriles*

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MNDO molecular orbital calculations are reported for the reaction of BH_3 with HCN. The results indicate that the reaction proceeds exothermally via an intermediate linear complex, with an activation barrier of 21 3 kcal/mol In the gas phase, the reaction is shown to proceed in two stages : the formation of the linear complex and its rearrangement to the product via intramolecular hydrogen migration The adduct has a donor-acceptor type of bond between nitrogen and boron The possibility of an alternative mechanism, involving the direct attack of the carbon-nitrogen π-bond by borane, resulting in a π-complex having a three-center two-electron bond, as in the case of acetylene (which has a homopolar triple bond), has been eliminated. Charge transfer effects have also been discussed.

RECENTLY, the hydroboration reaction has attracted the interest of a large number of theoretical chemists[1-6]. Most of these studies were, however, confined to the hydroboration reactions of alkenes and alkynes. Similar reactions are also shown by heteropolar double and triple bonds[7,8]. The hydroboration of organic nitriles is of particular importance since it provides a convenient route to the synthesis of amines. In view of this, we decided to carry out a study of this reaction to determine the nature of the stationary points on the reaction surface, and the activation energy barrier for the reaction.

Method of calculation: The MNDO method with the usual parameters[9,10] was used for all the molecular orbital calculations reported here. Equilibrium geometries were optimized using the Davidon-Fletcher-Powell method[11].

The transition state geometry was located by the energy minimization method, using the length of the forming C-H bond as the reaction coordinate. Rothman and Lohr[12] have pointed out that the maxima obtained on such reaction surfaces are saddle points, provided the reaction pathway is continuous in that region. According to these authors[12] the force constant matrix at such points has one, and only one, negative eigen value.

Results and Discussion

The product of the hydroboration of nitriles contains the boron atom bonded to the nitrogen.



$$RCN + BH_3 \rightarrow RCHNBH_2$$

In the present work, we have studied the energy profile for this reaction. For the sake of simplicity we have studied only the case for R=H.

A CNDO/2 study of this reaction by Datta *et al*[3] indicated that it proceeds through a transition state having a three-center bond. In the course of our present calculations, we found that a three-center geometry is neither a transition state, nor an intermediate. There is no three-center stationary point on the reaction surface. In fact, diborane is a Lewis acid which functions best as a reducing agent in attacking groups at positions of high electron density, such as the nitrogen atom of the nitrile group, which is relatively basic. This nitrogen is known to add to boron trifluoride to form addition compounds of moderate stability[13]. Presumably, the rapid reduction of nitriles by diborane involves an initial attack of this reagent on this relatively basic position, as originally suggested by Brown and Subba Rao[14]. We first identified the product of the reaction. Optimization of the geometry, keeping the BH_2 group in the same plane as the $\substack{H\\H}\!>$C-N group, gives a structure having a heat of formation of 19 2 kcal/mol and a CNB angle of 124 4° However, if the BH_2 group is allowed to rotate about the B-N bond, the geometry optimizes to a structure having the BH_2 group normal to the plane of the CH_2 group and a heat of formation of 5.2 kcal/mol Surprisingly, the CNB bonds also become linear. This structure (P), is shown in Fig. 1.

The reaction profile is shown in Fig. 2. There are two transition states and one intermediate along the reaction path. The linear adduct is initially formed as a stable intermediate. The activation energy required for its formation is 3.8 kcal/mol. The optimized geometries of the transition state (T1) and the adduct (A) are shown in Fig. 1. The adduct (A) is more stable than the reactants by 19.8 kcal/mol. The second step in the reaction is the

* Dedicated to Prof. R. C. Mehrotra on the occasion of his 60th birth anniversary.

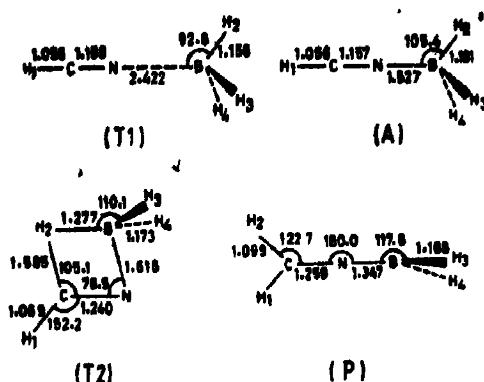


Fig. 1. Optimized geometries (in angstroms and degrees) of the transition state (T1) for the formation of adduct, the adduct (A), the transition state (T2) for the formation of product and the product (P)

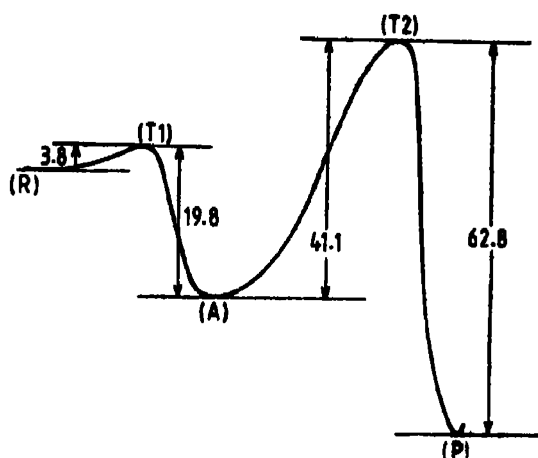


Fig. 2. The energy profile (kcal/mol) for the reaction of HCN with BH_3

rearrangement of the adduct to the product This requires an activation energy of 41 1 kcal/mol This is thus the rate-determining step The transition state (T2), shown in Fig 1, has a four-center-like structure.

The overall activation energy for the reaction is thus 21.3 kcal/mol. Although the experimental gas phase value for the activation energy is not available, our value seems reasonable. Brown and Korytnyk[15] had observed that, in solution, nitriles are less reactive than olefins towards hydroboration The MNDO calculated[9] barrier for hydroboration of ethylene is 7.6 kcal/mol. The enthalpy of hydroboration of HCN is found to be -41.5 kcal/mol and the reaction is exothermic. On going from the reactant to the product, the B-N bond distance at first decreases until the linear adduct is formed. It then increases to a value of about 1.7Å, after which it decreases to its value of 1.35Å for the product. Similarly, the CNB angle remains constant at 180° until the linear adduct is formed, after which it decreases to a value of 76.4° near the second transition state, T2. The CNB bond angle then increases, until it becomes linear in the product.

Charge transfer effects : It is also pertinent to examine the charge transfer effects accompanying the above-mentioned reaction. In Table 1, we have given the charges on various atoms in the reactants (R), at the transition state (T1) for the formation of adduct, at the adduct (A), at the transition state (T2) for the formation of product, and at the product (P). There is a very negligible change in the charges on going from the reactants to T1. At T1, only 0.03 units of electronic charge is transferred from the HCN moiety to the BH_3 moiety. Therefore, it resembles the reactants more closely than the adduct (A). As the reaction proceeds from T1 to A, there is a negligible effect on the hydrogens, but the carbon, nitrogen and boron atoms reverse their charges In the adduct, 0.38 units of charge is transferred from the HCN moiety to the BH_3 moiety Of this, 0 20 units of charge come from the nitrogen, while the carbon atom donates about 0 14 units of charge to the boron. In T2, the amount of transfer reduces to 0.23 units. This is mainly due to back donation of charge to the nitrogen and the hydrogen of the HCN moiety In the product, the nitrogen atom becomes more negatively charged, while the carbon becomes more positively charged The boron atom again becomes positively charged. As the reaction proceeds from T2 to P, there is transfer of charge from boron to nitrogen.

Table 1 – Charges on Various Atoms in the Stationary Points on the Reaction Surface (see Fig. 2)

Atom[a]	Charge (Q) R	T1	A	T2	P
H_1	0.19	0 20	0 23	0.17	0 03
C	−0 09	−0 05	0 05	0 14	0.23
N	−0.10	−0.12	0.10	−0 08	−0.33
B	0 24	0 21	−0 17	−0 17	0 06
H_2	−0 08	−0 08	−0 07	−0 06	0.03
$H_{3,4}$	−0 08	−0 08	−0 07	0 00	−0 01

[a] See Fig 1 for numbering of hydrogens

Conclusions : Our calculations have indicated that the hydroboration of hydrogen cyanide proceeds in two stages The first is the formation of the linear adduct and the second is its rearrangement to the product The latter is the rate-determining step The reaction is exothermic and has a large negative enthalpy. The possibility of the reaction taking place via a three-center intermediate or transition state, as suggested by Datta *et al*[8], is completely ruled out. The intermediate complex is found to be linear and the transition state has a four-center-like structure. The intermediate complex is much more stable than the reactants. The overall mechanism proposed from the results of the present theoretical study is in agreement with that originally suggested by Brown and Subba Rao[14].

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Diisothiocyanatodihalonickelates(II)

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Few diisothiocyanatodihalonickelates(II) $R_2[Ni(NCS)_2X_2]$ [$R=(C_6H_5)_4As$, $(C_6H_5)_4P$ or $(n\text{-}C_3H_7)_4N$ and X = Cl, Br or I] have been isolated from non-aqueous media and characterized by chemical analyses, melting points, molar conductance, ir and far ir and electronic spectral studies.

WE have been interested in the study of mixed halometallates viz., mixed haloantimonates(III)[1,2] and mixed halocobaltates(II) and nickelates(II)[3-6] and also substituted mixed halometallates of cobalt(II)[7] and nickel(II)[8]. Simple tetrahalo- and tetraisothiocyanatonickelates(II) $(NiX_4)^{2-}$ (X=Cl, Br, I or SCN) are well known[9,10] and there has also been reports on mixed tetrahalonickelates(II)[11,12] but study on tetracoordinated nickelates(II) containing both halogens and thiocyanate groups is scanty[13]. In this article, we are reporting the isolation and ir, far ir and electronic spectral studies of $R_2[Ni(NCS)_2X_2]$ [$R=(n\text{-}C_3H_7)_4N$, $(C_6H_5)_4As$ or $(C_6H_5)_4P$ and X=Cl, Br or I].

Experimental

Preparation: These complexes were prepared by the interaction of nickel thiocyanate (prepared in absolute ethanol by the metathetical reaction of $Ni(NO_3)_2.6H_2O$ and KNCS (1 : 2) in presence of a small amount of triethylorthoformate) and R_4MX ($R=C_6H_5$ or $n\text{-}C_3H_7$; M=N, P or As and X=Cl, Br or I) in 1 : 2 molar ratio in a 2 : 1 (v/v) mixture of acetonitrile and absolute ethanol. The crystals thus obtained were recrystallised from acetonitrile, filtered, washed with a small amount of acetonitrile and then with ether and dried in an air oven at 90-100°.

Analyses: All the complexes were analysed for total thiocyanate plus halogen contents gravimetrically as AgSCN plus AgX (X=Cl, Br or I) and also separately for thiocyanate contents by oxidizing SCN to sulphate by bromine water and precipitating as $BaSO_4$. Carbon and hydrogen were analysed at C.D.R.I., Lucknow. The melting points and analytical results are given in Table 1.

Physical measurements: Conductance measurements were carried out on $\sim10^{-3}$ *M* solutions in nitromethane using a conductivity bridge made by PYE W.G & Co. Ltd., (England). The electronic spectra were recorded as nujol mulls on Unicam SP 700 spectrophotometer. IR spectra (400-4000 cm^{-1}) were recorded as nujol mulls on Unicam SP 1200 spectrophotometer. The far ir spectra (400-50 cm^{-1}) were recorded as nujol mulls using polythene discs on Perkin Elmer 180 spectrophotometer.

Results and Discussion

Conductance measurements: The molar conductance values ($ohm^{-1}\ cm^2\ mol^{-1}$) of these complexes (Table 1) (at $\sim10^{-3}$ *M*) in nitromethane (at 25±1°) fall within the generally acceptable range[14] for 2 : 1 electrolytes (Λ_M=150-180) indicating them to be 2 : 1 electrolytes.

IR spectra (400-4000 cm^{-1}): The observed ν CN ($\sim$2090 cm^{-1}), ν CS ($\sim$825 cm^{-1}) and δ NCS

TABLE 1 – ELEMENTAL ANALYSES, MELTING POINTS AND MOLAR CONDUCTANCE ($ohm^{-1}\ cm^2\ mol^{-1}$)

Compound	Elements present	% Found	% Calcd.	m p. (°C)	Λ_M in $10^{-3}M$ CH_3NO_2
$[(C_6H_5)_4As]_2[Ni(NCS)_2Cl_2]$	C	58 8	59.3	224-6	172
	H	3 8	3 9		
	Cl	6 7	7 0		
	SCN	11 8	11 5		
$[(C_6H_5)_4As]_2[Ni(NCS)_2Br_2]$	C	55 2	54.5	254-6	175
	H	3 7	3.6		
	Br	14 1	14 5		
	SCN	10 6	10 5		
$[(C_6H_5)_4P]_2[Ni(NCS)_2Br_2]$	C	58 9	59 2	266-8	171
	H	3 6	3 9		
	Br	15 4	15.8		
	SCN	11 7	11.4		
$[(n\text{-}C_3H_7)_4N]_2[Ni(NCS)_2I_2]$	C	38 4	38 9	160-2	167
	H	7 2	7.0		
	I	30.2	31.7		
	SCN	14 2	14.5		

TABLE 2 – IR SPECTRAL DATA (4000-400 cm^{-1})

Compounds	δNCS	νCS	νCN	2δNCS
$[(C_6H_5)_4As]_2[Ni(NCS)_2Cl_2]$*	–	820 m	2085 vs	952 w
$[(C_6H_5)_4As]_2[Ni(NCS)_2Br_2]$*	–	825 m	2090 vs	952 w
$[(C_6H_5)_4P]_2[Ni(NCS)_2Br_2]$	475	826 m	2091 vs	945 w
$[(n\text{-}C_3H_7)_4N]_2[Ni(NCS)_2I_2]$	470 m	824 m	2092 vs	948 w

* δ NCS absorption is masked by strong absorption due to Ph_4As^+ cation in this region.
m = medium, w = weak, vs = very strong.

(~470 cm^{-1}) frequencies (Table 2) occur in the frequency ranges[10] suggested for the N-bonded thiocyanate ligand. The first overtone of NCS is also observed at ~950 cm^{-1}.

Far ir spectra : On the basis of C_{2v} symmetry of $[Ni(NCS)_2X_2]^{2-}$ there should appear two Ni-X and two Ni-N stretching and one bending mode each for X-Ni-X and N-Ni-N As regard the assignment for N-Ni-N bending mode there is no report even for $[Ni(NCS)_4]^{2-}$ species[15]. Recently, Engelter and Thornton[16] have assigned a band at 165 cm^{-1} to N-Zn-N bending mode in $ZnPy_2(NCS)_2$ by applying isotopic substitution method On this basis, in present case bands around 165 cm^{-1} have been tentatively assigned to N-Ni-N bending mode The band positions and their assignments are given in Table 3.

TABLE 3 – FAR IR (400-50 cm^{-1}) SPECTRAL DATA

Compounds	Peak position	Assignment
$A_2[Ni(NCS)_2Cl_2]$	298 s	
	283 s	ν (Ni-Cl) + ν (Ni-N)
	236 m, 187 m	
	86 m, 71 ms	cation
	156 m	δ (N-Ni-N)
	127 w	δ (Cl-Ni-Cl)
$P_2[Ni(NCS)_2Br_2]$	300 s, 277 s	ν (Ni-N)
	245 s, 238 sh	ν (Ni-Br)
	267 m, 200 w	cation
	147 w, 70 m	
	167 m	δ (N-Ni-N)
	84 w	δ (Br-Ni-Br)
	180 m	unassigned
$A_2[Ni(NCS)_2Br_2]$	296 s, 276 s	ν (Ni-N)
	237 s, 224 sh	ν (Ni-Br)
	202 m	unassigned
	164 w	δ (N-Ni-N)
	82 w	δ (Br-Ni-Br)
	182 m	cation
$Pr_2[Ni(NCS)_2I_2]$	297 s, b	ν (Ni-N)
	198 s, b	ν (Ni-Cl)
	162 w	δ (N-Ni-N)
	70 m, 58 m	δ (I-Ni-I) or cation

A = $(C_6H_5)_4$ As ; P = $(C_6H_5)_4P$; Pr = $(n\text{-}C_3H_7)_4N$
s = strong ; ms = medium strong ; m = medium ; w = weak ; sh = shoulder ; b = broad.

In case of $[Ni(NCS)_2Cl_2]^{2-}$ instead of the expected four stretching bands (two ν Ni-Cl and two ν Ni-N), only two broad bands are observed (298, 283 cm^{-1}) in this region, which may be due to the fact that νNi-N and νNi-Cl absorptions occur in nearly the same region of the spectrum[15,17]. However, it is not possible to distinguish as to which band is due to which vibration. The band at ~156 cm^{-1} has been tentatively assigned to δ N-Ni-N[16] and that at 127 cm^{-1} to δ Cl-Ni-Cl[17].

In case of $[(C_6H_5)_4P]_2$ $[Ni(NCS)_2Br_2]$, two bands at 300 and 277 cm^{-1} have been assigned to two Ni-N and those at 245 and 238 cm^{-1} to two Ni-Br stretching modes. These values are in good agreement with those reported for $[Ni(NCS)_4]^{2-}$ and $(NiBr_4)^{2-}$ species[15,17,18]. The bands at 167 and 86 cm^{-1} have been assigned to δ N-Ni-N and δ Br-Ni-Br[16,17] Similar assignments could be made for $[(C_6H_5)_4As]_2$ $[Ni(NCS)_2Br_2]$ (Table 3).

In the spectrum of $[Ni(NCS)_2I_2]^{2-}$ Ni-N and Ni-I stretching absorption bands do not show any splitting, instead they appear as single broad bands at 297 and 198 cm^{-1} respectively. The weak band at 162 cm^{-1} has been assigned to N-Ni-N bending mode[16,17], whereas those at 70 and 58 cm^{-1} may be due to either I-Ni-I bending mode[17] or cation, as the latter also absorbs in this region.

Electronic spectra : On the basis of C_{2v} symmetry of $[Ni(NCS)_2X_2]^{2-}$, bands corresponding to the ν_2 and ν_3 transitions in tetrahedral Ni(II) should exhibit some splitting[19,20]. But in the present case the visible region bands (ν_3)(14800-16200 cm^{-1}) (Table 4) do not show any splitting indicating

TABLE 4 – ELECTRONIC SPECTRAL DATA

Compounds	Band position (cm^{-1})	10 Dq (cm^{-1})	B' (cm^{-1})	β(= B'/B)
$[(C_6H_5)_4As]_2[Ni(NCS)_2Cl_2]$	16130b	4320	799	0.776
	8547			
	5650			
	5050b			
$[(C_6H_5)_4As]_2[Ni(NCS)_2Br_2]$	15385b	4160	683	0.663
	9389			
	5730b			
	5050			
$[(n\text{-}C_3H_7)_4N]_2[Ni(NCS)_2I_2]$	14815b	4000	653	0.633
	8510			
	6135			
	5634			
	5071			

b = broad

that the low symmetry has no effect in splitting the ν_3 band in T_d symmetry. Such a situation has also been observed in case of mixed tetrahalonickelates(II)[18] $(NiCl_2Br_2)^{2-}$. However, the lowest energy band in near ir region (5050-6100 cm^{-1})

except in $[Ni(SCN)_2I_2]^{2-}$ are rather broad, which may be assumed as consisting of split components (but not well resolved) of the ν_2 band. The highest energy band in the near ir region (8500–9400 cm^{-1}) appears as a single band which has been assigned to ν_2 transition in simple T_d symmetry of Ni(II).

The ligand field parameters calculated by adopting tetrahedral model using equations employed by Underhill and Billing[21] are given in Table 4. All the parameters indicate that the crystal field strength lies in the order $I^- < Br^- < Cl^-$. The B′ values compared to that of free ion [1030 cm^{-1} for Ni(II)] suggest the presence of an appreciable orbital overlap which lie in the order $I^- > Br^- > Cl^-$.

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Polarographic Studies on Acidic Aminoacid Imines (N-Salicylidene-l-aspartic Acid and N-Salicylidene-l-glutamic Acid)

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Polarographic studies of N-salicylidene-l-aspartic acid and N-salicylidene-l-glutamic acid have been made at the DME at different pH, temperatures, concentrations and in the presence of some surfactants in aqueous B R buffers, at constant ionic strength Single well-defined cathodic irreversible waves were observed for which two-electron reduction mechanism with radical anion formation has been proposed.

ASPARTIC and glutamic acids being acidic amino acids, play a major role in biological processes like transamination[1], decarboxylation[2], cell metabolism[3] and neurotransmission[4] reactions The biological importance of amino acid imines was recognized by Metzler, Ikawa and Snell[5].

Zuman[6] has given an indirect polarographic method for the estimation of amino acids by converting them into suitable imines which are easily reducible at the dropping mercury electrode (dme).

The polarographic reduction of various, substituted imines has been investigated earlier[7-9]. In the present communication, we report polarographic reduction studies of N-salicylidene-l-aspartic acid (NSA) and N-salicylidene-l-glutamic acid (NSG) at the dme. The influence of *p*H, temperature, concentration, mercury pressure and surfactants has been studied which has thrown light on their mode of reduction.

Experimental

NSA and NSG were prepared by the method given by Smith[10] in which piperidine, was used as a base catalyst The synthesis was confirmed by spot reactions and ninhydrin test ; the purity of compound was checked by tlc wherein only one spot was observed. In spectral studies the uv peaks were observed at 287 and 289 nm for NSA and NSG respectively which are characteristic of >C=N– linkage[11]. The ir absorption peaks were similarly observed at 1600 and 1630 cm^{-1} for NSA and NSG respectively. The imines were also characterized by elemental analysis for molecular formula $C_{11}H_{11}O_5N$ for NSA, m.p. 478°K and for molecular formula $C_{12}H_{14}O_5N$ for NSG, m.p. 497°K.

Polarograms were recorded with a Toshniwal manual polarograph No. 039 using a saturated calomel electrode (SCE) as the reference electrode. The capillary of the dropping mercury electrode had the following characteristics :

$m = 1.55$ mg S^{-1} ; $t = 3.53$ S at $E = -1.10$ V vs SCE in closed circuit and $m^{2/3} t^{1/6} = 1.652$ $mg^{2/3}$ $S^{-\frac{1}{2}}$.

Deaeration was carried out by passing pure oxygen-free nitrogen in the polarographic cell for about 20 min before the study and subsequently an atmosphere of nitrogen was maintained over the test solution. Aqueous solutions of imines were prepared in freshly double distilled water.

Results and Discussion

Influence of pH : NSA and NSG gave single well defined waves at all the *p*H values ranging from 2.1 to 11.0. NSA gave a sharp maximum at *p*H 2 10 which was suppressed by the addition of 0 002% Triton X-100. The slope values of the log plot analysis for both the imines are recorded in Table 1.

TABLE 1 – CHARACTERISTICS OF POLAROGRAPHIC WAVES OF N-SALICYLIDENE-l-ASPARTIC ACID (NSA) and N-SALICYLIDENE-l-GLUTAMIC ACID (NSG)

B R buffer medium; Ionic Strength I = 0 5; Conc = 2.56×10^{-4} *M*; Temp. = 303° ± 0 1° K

*p*H	$-E_{\frac{1}{2}}$ volts vs S C E.	i_l in μA	Slope values of log plots in V
N-Salicylidene-l-aspartic acid (NSA)			
2 10	1 045	1 460	0 058, 0.044
4 20	1 185	2 133	0.050
7.17	1 330	1 200	0 072
9 17	1 470	4 133	0.062
11.02	1.770	6.800	0.074
N-Salicylidene-l-glutamic acid (NSG)			
2 10	1.030	0 933	0.090
4.20	1.190	2.133	0.054
7.17	1.320	1.500	0.066, 0.052
9.17	1.482	7.200	0.068, 0.042
11.02	1.820	4.400	0.044, 0.036

* Senior author to whom all the correspondence should be made.

Typical polarograms of $2.56 \times 10^{-3} M$ concentrations are recorded in Figs. 1 and 2.

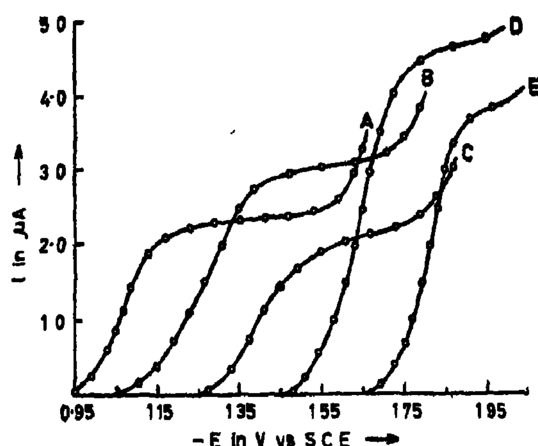


Fig. 1 Polarographic curves of N-salicylidene-l-aspartic acid in aqueous B R buffer at 0 5 ionic strength · A pH 2 10, B 4 20, C 7 17; D 9 17; E-11 02, Conc 2 56 mM.

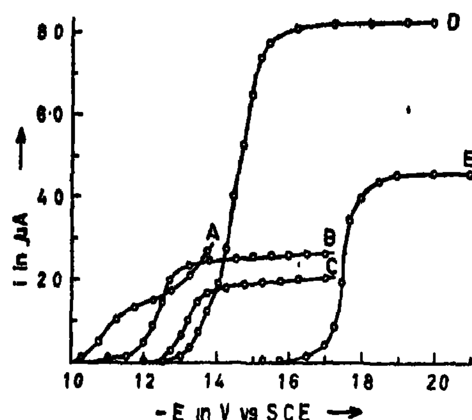


Fig 2. Polarographic curves of N-salicylidene-l-glutamic acid in aqueous B R. buffer at 0.5 ionic strength A pH 2 10, B 4.20; C 7.17, D 9.17, E 11 02, Conc. 2 56 mM

Influence of concentration: Studies were made at depolarizer concentration of 2.56 to 9 52 mM in B R. buffer from *pH* 2 10 to 11 02 at I=0 5. The i_l/C values varied with concentration in a peculiar manner. The results are recorded in Table 2.

TABLE 2—RELATION BETWEEN LIMITING CURRENT AND DEPOLARIZER CONCENTRATION

Conc. mM	i_l/C at different pH values: pH 2.1	4 2	7.2	9.2	11.0
N-Salicylidene-l-aspartic acid (NSA)					
2.56	0.607	0.834	0.478	1.714	1.023
5.00	0 384	0 532	0.352	1.649	1.361
7.31	0.307	0.479	0 312	1.621	1.417
9.52	0.284	0.375	0.201	1.605	1.197
N-Salicylidene-l-glutamic acid (NSG)					
2.56	0.405	0.829	0.603	3.161	1.004
5.00	0.254	0.458	0.926	2.846	0.625
7.31	0.353	0.331	0.792	2 637	0 803
9.52	0.425	0.630	0.850	2.530	0.902

Influence of mercury pressure: The experiments were made in the range of 20 to 60 cm height of mercury column at selected *p*H range in B.R. buffer at 303° ± 0.1° K. The $i_l/h^{\frac{1}{2}}$ corr. values decreased with increasing height in each case.

Influence of temperature: The influence of varying the temperature was studied at *p*H 4.0, I=0.5 between 303° K and with intervals of 5°. The values of temperature coefficient varied from 2 69 to 3.02 for NSG and 2 54 to 3.10 for NSA.

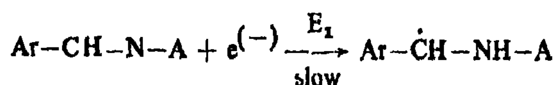
Influence of surfactants: Camphor or thymol was added to the test solution. On increasing the concentration of camphor or thymol, the wave heights decreased gradually and the $E_{\frac{1}{2}}$ of the waves shifted towards negative potentials.

These imines are biprotic, tridentate ligands which contain a phenolic hydroxy group, two carboxylic groups, phenyl ring and an imine linkage >C=N−. The -OH group is located at the *ortho* position to the imine linkage which leads to an increase in the charge density on >C=N− or imine linkage. The possible reduction site in the molecule is the azomethine linkage where the presence of a lone-electron pair on nitrogen makes the molecule susceptible to reduction.

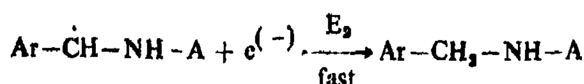
At low *p*H values the presence of -COOH groups facilitate the reduction of imine linkage at less negative potentials whereas at higher *p*H, a shift in $E_{\frac{1}{2}}$ to more negative potential is observed due to the formation of -(COO⁻) carboxylate ion and the presence of -OH group. The negative shift of $E_{\frac{1}{2}}$ values with increasing *p*H indicates the involvement of protons[12]. The -OH groups does not partake in electroreduction as it forms intramolecular hydrogen bonding with imine lnkage with resulting mesomeric effect[13] in the molecule.

The high log-plot slope values indicate irreversible nature[14] of the electrode process. Further, the limiting current values do not appear to increase in proportion to the concentration. The values of $i_l/h^{\frac{1}{2}}$ corr., also decrease with increasing mercury pressure. All these observations indicate that the reduction is kinetically controlled[15] at least partially. The plot of $E_{\frac{1}{2}}$ vs *p*H values in each case, do not yield a straight line but the points lie on two straight lines. The average variation of $E_{\frac{1}{2}}$ for NSA per *p*H unit was found to be 0.06 volt in acidic *p*H range and 0.09 volt per *p*H unit in alkaline media, whereas the average variation of $E_{\frac{1}{2}}$ for NSG per *p*H unit is 0.06 volt in acidic *p*H and 0.08 volt in alkaline *p*H. These facts indicate that proton is involved in each step of reduction.

On the basis of the foregoing facts, the mechanism of reduction of both the imines can be represented as follows ;



$$Ar-CH-N-A + e^{(-)} \xrightarrow[\text{slow}]{E_1} Ar-\dot{C}H-NH-A$$



$$Ar-\dot{C}H-NH-A + e^{(-)} \xrightarrow[\text{fast}]{E_2} Ar-CH_2-NH-A$$

where Ar = carbonyl residue and A = coupled amino acid residue.

The first step is slow and rate determining.

Such electron transfer processes have been evaluated earlier also[16] and similar mechanism has been proposed by Scott and Jura[17] for the reduction of aromatic Schiff's bases.

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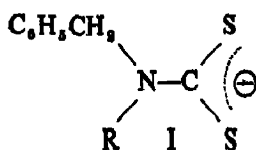
Oxomolybdenum(V) and Oxomolybdenum(VI) Complexes of Some New Dithiocarbamates

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Synthesis and characterisation of μ-oxo-di [bis(dithiocarbamato)oxomolybdenum(V)] and bis(dithiocarbamato)dioxomolybdenum(VI) with some new dithiocarbamato ligands of the type $RR'NCS_2^-$, where $R=C_6H_5CH_2$ and $R'=H$, CH_3, C_2H_5, $C_3H_7^i$ and $C_6H_5CH_2$, have been reported.

MOLYBDENUM is an important trace element in living organisms. Oxomolybdenum(V) and oxomolybdenum(VI) have recently been proposed as models for molybdenum coordination in enzymes[1,2]. In the present paper we report synthesis and characterization of some oxomolybdenum(V) complexes of the type $Mo_2O_3(dtc)_4$ and oxomolybdenum(VI) complexes of the type $MoO_2(dtc)_2$ with a series of new dithiocarbamato ligands I, viz., (i) benzylmethyl dithiocarbamate (BzMe-dtc), I_a; (ii) benzylethyl dithiocarbamate (BzEt-dtc), I_b; (iii) benzylisopropyl dithiocarbamate (BzisoPr-dtc), I_c and (iv) dibenzyl dithiocarbamate (Bz_2-dtc), I_d.



(a) $R=CH_3$, BzMe-dtc ; (b) $R=C_2H_5$, BzEt-dtc ; (c) $R=i\text{-}C_3H_7$, BzisoPr-dtc and (d) $R=C_6H_5CH_2$, Bz_2-dtc

Moore and Larson[3] had earlier reported difficulty in isolating pure oxomolybdenum(VI) complexes with larger and branched chain alkyl groups, viz., isopropyl and benzyl.

Experimental

A. *Preparations* : Sodium, potassium or ammonium salts of the dithiocarbamates were prepared by earlier described methods[4].

(i) $Mo_2O_3(dtc)_4$: For preparing the complexes of this type solution of the dithiocarbamato ligand (0.004 mol, aqueous or aquo-ethanolic) was added to a freshly prepared aqueous solution of $(NH_4)_2$-$MoOCl_5$ (0.002 mol) with stirring. The complexes were thrown out in each case, which were filtered, washed with water and vacuum dried over P_2O_5.

(ii) $MoO_2(dtc)_2$: For preparing the complexes of this type a solution containing sodium acetate (2 g), $Na_2MoO_4.2H_2O$ (0.010 mol) and the dithiocarbamato ligand (3.65 g ; 0.010 mole) in 250 ml of 50% ethyl alcohol was acidified by dropwise addition of 2 *M* nitric acid with stirring at 0° to adjust the *p*H to ~5.5 The complex precipitated out in each case which was filtered out, washed with cold water and dried in *vacuo* over P_2O_5. The dried solid was recrystallised from CH_2Cl_2-petroleum ether/cyclohexane

The complexes are soluble in $CHCl_3$ and CH_2Cl_2. An unpurified sample attained a slight purple tinge in a few days, probably getting reduced to molybdenum(V) species. The recrystallised sample was found to be stable over a period of one year.

B. *Physical measurements :* Magnetic susceptibility measurements on solid complexes were made by Gouy method using mercury tetrathiocyanatocobaltate(II) as calibrant

$$(\chi_g=16.4\times10^{-6} \text{ cgsu})$$

Infrared spectra in KBr pellets were recorded on Perkin-Elmer 621 and Perkin-Elmer 137 spectrophotometers. Visible spectra were recorded on Beckman DU-2 spectrophotometer.

Results and Discussion

A. $Mo_2O_3(dtc)_4$: All the complexes are diamagnetic. $Mo_2O_3(dtc)_4$ complexes are crystallographically[5,7] known to have two $MoO(dtc)_2$ units joined by a bridging oxygen atom, the Mo=O bonds of both units being on the same side. In mono-oxygen bridged complexes spin pairing occurs via the bridging oxygen atom, which leads to diamagnetism[8-11].

The visible spectra of the complexes show two strong bands around 24000 cm^{-1} and 19000 cm^{-1} (Table 1). The 24000 cm^{-1} band is assignable to L→M charge transfer[8,12,13]. In Mo_2O_3-$(Me_2dtc)_4$ and $Mo_2O_3(Et_2dtc)_4$ this absorption occurs[8] at 2000 cm^{-1} higher than in the present

TABLE 1—COMPOSITION AND λ_{max} OF THE COMPLEXES

Sl. No.	Compound*	Colour	m. p. °C	Found (Calcd.) C%	Found (Calcd.) H%	Found (Calcd.) N%	Found (Calcd.) Mo%	λ_{max} (cm^{-1}) in CH_2Cl_2 (log ε)
1.	$Mo_2O_3(Bz_2\text{-dtc})_4$	purple violet	84° dec.	54.53 (54.22)	4.00 (4.22)	3.90 (4.12)	14.83 (14.45)	24100 (3.48) 19010 (3.82)
2.	$Mo_2O_3(BzMe\text{-dtc})_4$	purple violet	96°	41.80) (42.19)	3.72 (3.90)	5.00 (5.47)	18.98 (18.47)	24630 (3.40) 19080 (3.44)
3.	$Mo_2O_3(BzEt\text{-dtc})_4$	purple violet	112° dec.	44.00 (44.45)	4.60 (4.44)	4.88 (5.19)	17.50 (17.77)	23360 (3.10) 19080 (3.01)
4.	$Mo_2O_3(Bz\ isoPr\text{-dtc})_4$	purple violet	89° dec.	45.84 (46.48)	4.80 (4.93)	4.80 (4.93)	17.00 (16.89)	24210 (3.37) 19080 (3.44)
5.	$MoO_2(Bz_2\text{-dtc})_2$	yellow	157° dec.	53.00 (53.58)	4.30 (4.17)	3.80 (4.17)	14.55 (14.28)	27550 (3.99) 26320 (4.00) 24100 sh
6.	$MoO_2(BzMe\text{-dtc})_2$	orange yellow	153-155° dec	40.90 (41.54)	3.70 (3.85)	4.90 (5.39)	18.32 (18.45)	26320 (3.62)
7.	$MoO_2(BzEt\text{-dtc})_2$	orange yellow	68-70°	43.28 (43.87)	4.08 (4.38)	5.32 (5.11)	17.30 (17.51)	23810 (3.21)
8	$MoO_2(Bz\ isoPr\text{-dtc})_2$	yellow	161° dec	45.60 (45.84)	4.78 (4.86)	5.02 (4.86)	16.30 (16.65)	23310 (3.09)

* ligands abbreviated as in the text.

complexes. This suggests that benzyl derivatives are better reducing agents than dialkyldithiocarbamates, as also is evidenced from the fact that the Mo(VI) complexes of the present ligands are difficult to prepare. Moore and Larsen[3] have earlier observed that S→Mo charge-transfer in xanthate complexes appear at 6000 cm^{-1} below that of the corresponding dithiocarbamate complexes and have suggested that xanthates are much better reducing agents than dithiocarbamates Also no Mo(VI) complex of xanthates is known

The 19000 cm^{-1} band is characteristic of the linear Mo-O-Mo bridge and is assigned to a transition terminating in the antibonding component of the three centre Mo-O-Mo bond[2,14,15]

All the $Mo_2O_3(dtc)_4$ complexes show an earlier reported[2,15] behaviour that the colour of their CH_2Cl_2 solution changes from purple through orange to yellow on standing. This colour change is accompanied with weakening of the 19000 cm^{-1} band which finally disappears. The phenomenon has now been proved definitively to be due to the following equilibrium in solution[2,14,15,21] :



$$Mo_2O_3(dtc)_4 \rightleftharpoons MoO_2(dtc)_2 + MoO(dtc)_2$$

All $Mo_2O_3(dtc)_4$ complexes show one strong band in the range 920-935 cm^{-1} which is assigned to both symmetric and antisymmetric terminal Mo=O stretching[16] modes (ν_t^s and ν_t^a). The above assignment is based on the work of Newton and McDonald, who studied the infrared spectra of ^{16}O and ^{18}O analogs of $Mo_2O_3(dtc)_4$ to conclude that a single band at 945 ± 15 cm^{-1} represents both symmetric and antisymmetric Mo-O_t stretching frequencies[16]. Spectra of all the complexes also show a medium intensity band at 420 cm^{-1} due to symmetric Mo-O-Mo stretching mode[16]. The antisymmetric Mo-O-Mo stretching band[16] could be observed only in $Mo_2O_3(BzMe\text{-dtc})_4$ (at 742 cm^{-1}), while in all other complexes strong ligand absorptions obscure this band

A strong band in the range 1470-1505 cm^{-1} is due to CN stretching mode. This band is observed in the range 1510-1550 cm^{-1} in the corresponding dialkyl derivatives[3]. The observed lowering in energy of this absorption in the present complexes may be explained as follows The presence of the benzyl group in the present complexes exerts an inductive effect, -I, by withdrawing electrons into the π-ring system of benzene This effect would decrease the double bond character of the CN bond

The $\nu^a_{(CSS)}$ and $\nu^s_{(CSS)}$ stretching frequencies in our complexes have been observed as strong bands in the regions 954-985 cm^{-1} and 688-700 cm^{-1} respectively. Medium to strong bands in the range 345-400 cm^{-1} are observed due to Mo-S stretching mode[2,14,16].

B *$MoO_2(dtc)_2$* : Moore and Larson[3] prepared dimethyl and diethyl derivatives by acidification with dilute hydrochloric acid, using the method of Malatesta[16] and reported that poor results were obtained with dithiocarbamates containing higher alkyl groups. The di-*n*-propyl derivative was prepared by using dilute nitric acid and the di-*n*-butyl derivative was prepared by oxidising the intermediate product with *t*-butyl hydroperoxide. The tendency to form a purple tar, believed to be the crude Mo(V) complex, increased with the increasing size of the alkyl group and pure Mo(VI) complexes with alkyl groups larger than *n*-butyl group could not be isolated. This instability is probably related

to the decreased electron releasing ability of the higher alkyl groups They also could not prepare di-iso-propyl derivative. It is quite encouraging that we got analytically pure yellow benzylisopropyl derivative, MoO_2(Bz isoPr-dtc)$_2$, using 1*M* HNO_3 and acetate buffer[10] at 0-5° In the case of MoO_2-(Bz_2-dtc)$_2$ and MoO_2 (BzMe-dtc)$_2$, the above method of preparation always resulted into the yellow Mo(VI) complex contaminated with some amount of purple coloured Mo(V). These two complexes and also MoO_2(BzEt-dtc)$_2$ were, therefore, prepared in aqueous ethanolic medium, taking advantage of the fact that Mo(VI) has an edge over Mo(V) in the presence of the organic solvents[9,18].

The electronic spectral bands for the complexes are listed in Table 1. All these bands are due to Mo ← S charge-transfer absorptions[18,19].

All the complexes show two strong bands one each in the regions 903-910 cm^{-1} and 870-875 cm^{-1}, assignable to the two Mo=O stretching modes[16]. The presence of two bands is consistent with the *cis*-dioxo structure of the MoO_2 group, which has been confirmed by crystallography for several MoO_2(dtc)$_2$ complexes[6,20].

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Mannich Bases as Potential Polydentate Ligands : 2,5-*Bis* (benzylaminomethyl) Hydroquinone Complexes

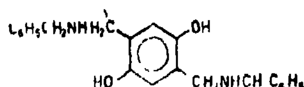
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The chelating properties of the Mannich base, 2,5-*bis*(benzylaminomethyl) hydroquinone (BAH) have been described. The ligand has been obtained by condensing 1 : 4 : 2 of hydroquinone, formaldehyde and benzylamine in dioxan medium The polymeric metal complexes, $[ML\ 2H_2O]_n$, where M = Co(II), Ni(II) and Cu(II), L = $C_{22}H_{22}N_2O_2$, have been synthesized by refluxing the metal ion and the ligand in 1 : 1 ratio in a medium of DMF The compounds are coloured powdery solids, insoluble in water and in common organic solvents Analytical, magnetic and spectral studies indicate an octahedral geometry for the complexes. The ligand field parameters have been reported

SCHIFF bases are known to have excellent chelating properties and their polydentate nature favours the formation of polymeric metal complexes. Though the formation of Mannich bases have been extensively investigated, no work appears to be on record on their complexes, inspite of the presence of favourable donors in suitable positions An attempt has been made to investigate the behaviour of Mannich bases as potential polydentate ligands and this communication records the results obtained in this direction.

The Mannich base, 2,5-*bis* (benzylaminomethyl) hydroquinone (BAH)[1,2] has been synthesized by the interaction of hydroquinone, formaldehyde and benzylamine Structure of the compound shows that it is capable of behaving as a tetradentate ligand, the donor atoms being the phenolic oxygens and imino nitrogens (I)



I. 2,5-*Bis*(benzylaminomethyl)hydroquinone (BAH)

However, all the donors cannot coordinate to a single metal ion, since they are not favourably located. Each metal ion is coordinated through a phenolic oxygen and an imino nitrogen of the ligand. Two metal ions are thus attached to two ends of the ligand and the coordination number of metal ion permits the attachment of further ligand molecules, so that a chain polymeric structure is obtained (II).

Experimental

Materials : Hydroquinone (B D.H.), benzylamine (E Merck), formaldehyde (B.D.H.) and the metal salts (B D.H), $Co(CH_3COO)_2\ 2H_2O$, $Ni(CH_3COO)_2.4H_2O$ and $Cu(CH_3COO)_2.H_2O$ were employed. Dimethylformamide, dioxan and other solvents used were of reagent grade.

Elemental analyses : Carbon, hydrogen and nitrogen were determined by microanalytical methods. The metal contents of the complexes were estimated by chelometric titration, after decomposition of the complexes by fuming HNO_3

Infrared spectra : Infrared spectra of BAH and its complexes were recorded on Aculab 10 Beckman Infrared spectrophotometer in the range of 4000-600 cm^{-1} using KBr pellets.

Reflectance spectra Diffuse spectra (uv/vis) in the solid state using MgO were recorded on VSU-2 spectrophotometer in the range 200-900 nm.

Magnetic measurements The magnetic susceptibility measurements were done by Faraday's method at room temperature (~298°K).

Preparation of ligand : The compound was prepared by the method described by Burke, Hammer and Weatherbee[1,2] . Formaldehyde (0 44 mol ; 33 ml, 37% aqueous solution) was mixed with 50 ml of dioxan cooled in ice, and benzylamine (24 ml ; 0 22 mol) was added dropwise with constant stirring. To the above, hydroquinone (11.0 g ; 0 10 mol) was added in small portions at a time, the mixture being stirred to ensure continuous dissolution of hydroquinone The solution was refluxed at about 100° for 2 hr when a white coloured product separated The mixture was cooled, the solid was filtered and recrystallised in methanol The purified product was dried and was hydrolysed by dilute hydrochloric acid (20 ml) on a sand bath, when all the solid dissolved. The solution on keeping overnight yielded a white powdery solid. This was then dissolved in water and liquor ammonia was added to precipitate the base. The precipitate was washed with water till free from chloride (Yield 76%).

Synthesis of metal complexes : BAH (3.48 g) dissolved in DMF (50 ml), was gradually added to a DMF solution of the metal salt [2.42 g of $Co(CH_3COO)_2.2H_2O$, 2.49 g of $Ni(CH_3COO)_2$.-

TABLE 1—COLOUR AND ANALYTICAL DATA

Compound	Colour	Elemental analyses % Found (Calcd.)			
		C	H	N	Metal
BAH($C_{22}H_{24}N_2O_2$)	White	75.80 (75 86)	6 58 (6 89)	8 04 (8.10)	— —
Co($C_{22}H_{22}N_2O_2$) $2H_2O$	Reddish brown	58.20 (59.82)	5 02 (5.90)	6.38 (6 40)	13.28 (13.36)
Ni($C_{22}H_{22}N_2O_2$) $2H_2O$	Greyish green	58 20 (59 80)	5.00 (5 88)	6.35 (6 42)	13.26 (13 32)
Cu($C_{22}H_{22}N_2O_2$) $2H_2O$	Brown	58.05 (59.20)	4 97 (5.83)	6 28 (6 32)	24.00 (14.24)

TABLE 2—INFRARED SPECTRA OF BAH AND ITS COMPLEXES (WAVE NUMBERS ARE IN cm^{-1})

BAH	Co(II)	Ni(II)	Cu(II)	Assignment
3360	—	—	—	νOH (phenolic)
—	3400	3400	3400	νOH (H_2O)
3290	3040	3040	3060	νNH
3260	2925	3020	2925	νNH
1680	1650	1660	1650	δNH
—	1630	1620	1600	δH_2O
1320	1270	1270	1270	νC-O

The magnetic moment values of the complexes show that all the three complexes are paramagnetic. From the magnetic moment values and reflectance spectra (Table 3) octahedral geometry is inferred. The various ligand field parameters which have been calculated, (Table 4) further confirm the geometry[3-5].

The infrared spectrum of BAH (Table 2 ; wave numbers are in cm^{-1}) shows a band at 3360 which may be assigned to hydrogen bonded OH (phenolic) stretching frequency. A medium band at 3260 is

TABLE 3—MAGNETIC MOMENTS AND REFLECTANCE SPECTRA

Complex	Magnetic moment (B.M)[a]	Positions of bands (cm^{-1})	Assignment	Geometry
Co(II)-BAH	5 02	10350	$^4T_{1g} \rightarrow {}^4T_{2g}$(F)	
		21550[b]	$^4T_{1g} \rightarrow {}^4A_{2g}$(F)	Octahedral
		22220	$^4T_{1g} \rightarrow {}^4T_{1g}$(P)	
Ni(II)-BAH	3 14	10270	$^3A_{2g} \rightarrow {}^3T_{2g}$(F)	
		15650	$^3A_{2g} \rightarrow {}^3T_{1g}$(F)	Octahedral
		27220	$^3A_{2g} \rightarrow {}^3T_{1g}$(P)	
Cu(II)-BAH	1.98	10000	$^2B_{1g} \rightarrow {}^2A_{1g}$	
		10869	$^2B_{1g} \rightarrow {}^2B_{2g}$	Octahedral
		11363	$^2B_{1g} \rightarrow {}^2E_g$	

a : B M. = $9.273 \times 10^{-24} m^2$, A

b : Calculated value.

$4H_2O$ or 2.00 g of Cu($CH_3COO)_2.H_2O$]. The mixture was refluxed over sand bath for 2-3 hr as necessary. The contents of the flask were cooled and the separated solid was filtered, washed successively with DMF and ether and dried over $CaCl_2$ under reduced pressure

The compounds are all air stable coloured powders, insoluble in water as well as in ethanol, acetone, chloroform, benzene and nitrobenzene. The colour and analytical data of the complexes are presented in Table 1, ir spectral data in Table 2, magnetic characteristics and DRS in Table 3.

Results and Discussion

The general empirical formula : ML.$2H_2O$ [where M=Co(II), Ni(II) and Cu(II) ; L=$C_{22}H_{22}N_2O_2$] for the complexes is indicated from analytical data (Table 1).

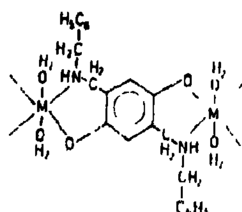
due to -NH stretching frequency and the band at 1320 to C-O stretching frequency. The spectra of complexes do not have the band of the free ligand at 3360, which indicates the involvement of phenolic oxygen in complexation, with deprotonation of the phenolic hydrogen[6,7]. The presence of a new strong band near 3400 in the complexes is due to OH stretching frequency of coordinated water.

TABLE 4—LIGAND FIELD PARAMETERS

Complex	10Dq (cm^{-1})	ν_2/ν_1	B' (cm^{-1})	β	β^o(%)
Co(II)-BAH	11200	2 1	848	0 96	13.7
Ni(II)-BAH	10270	1.52	12960	0.81	11.2

10 Dq = Crystal field splitting energy
B' = Racah's parameter
β = Measure of covalency
β^o = Percentage covalency

The OH deformation frequency at 1630 further shows the presence of H_2O[8]. The NH stretching frequency suffers a negative shift in the spectra of the complexes which indicates the coordination of nitrogen to the metal ion[9,10]. The C-O stretching frequency which is observed at a lower wave number in the complexes, further confirms the coordination of phenolic oxygen[11] to the metal ion with the formation of C-O-M bond The ir spectral data show that BAH acts as tetradentate chelating agent, coordinating through phenolic oxygens and imino nitrogens. All the four donors do not coordinate to the same metal ion due to steric factors, thus leading to the formation of polymeric[12-14] chain of BAH-metal linkages (II)



II Polymeric metal(II)-BAH complex, $[M \cdot 2H_2O]_n$

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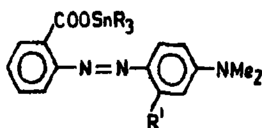
Formation of Unusual Molecular Complexes by Some Organotin(Aryl azo)benzoates

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Triorganotin-o-(4-N,N-dimethyl amino benzene azo)benzoates are characterised by an unusual ability to form molecular complexes with a wide variety of molecules including saturated hydrocarbons. Formation constants vary from ~10^{-3} litre mole^{-1} for the saturated hydrocarbon complexes to ~10^{3} litre mole^{-1} for chloranil complexes. The bathochromic shift of the π-π^* transition as well as the presence of CT band in nitrobenzene complex suggest these to be of donor-acceptor type, the organotin molecule behaving as the donor. Protonated species are formed by the action of protic solvents on the complexes. Possible reasons for the unusual donor ability is discussed.

FUNCTIONALLY substituted azobenzenes have been extensively used[1-3] for the synthesis of triorganotin complexes where the coordination number of the tin atom can be varied from 4 to 7 by using appropriately substituted azobenzene. Even the extremely rare 7-coordinated triorganotin chelates have been prepared using acetoxy substituted azobenzenes[4]. Amongst these group of compounds triorganotin-*o*-(4-N,N-dimethyl amino benzene azo)benzoates (I) are unique in their ability to form molecular complexes with almost any type of molecule including unsubstituted alkanes for which no example other than the contact charge transfer complexes(CCT) are known[5].



IA – R = Ph, R' = H
IB – R = *n*-Bu, R' = H
IC – R = Ph, R' = Me

I

In this paper we briefly discuss the evidences leading to the characterisation of such unusual molecular complexes which opens up the possibility of synthesising more stable complexes involving saturated hydrocarbons.

Experimental

Triorganotin complexes, IA and IB, were prepared by the method described by Majee and Banerjee[2].

IC was prepared by stirring at room temperature equimolar mixture of Ph_3SnCl and sodium salt of *o*-(2-methyl, 4-N,N-dimethyl aminobenzene azo)-benzoic acid in ethanol for about 10 hr. The product was recrystallised from petroleum ether; m.p. 144°, yield 70%.

Methyl ester of *o*-(4-N,N-dimethyl aminobenzene azo)benzoic acid (II) was prepared by the method described by Majee and Chakravarti[22].

All solvents were of Uvasol (E. Merck) grade. Optical densities were measured with a Beckman DU-2 spectrophotometer using 1 cm quartz cells. All measurements were carried at r.t. (27±2°).

All computations were carried on DCM Microsystem 1121 and Spectrum-I.

Results and Discussion

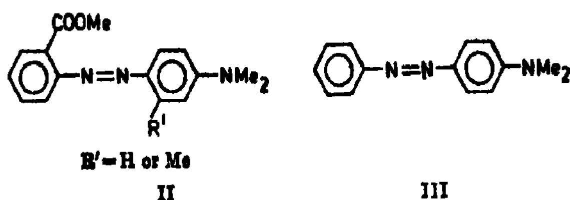
Electronic absorption spectra of aryl azo benzenes and their organotin derivatives: The electronic spectra of azobenzene and its derivatives are characterised by two bands, an intense absorption ($\epsilon_{max} \sim 10^4$) due to π-π^* transition and a weak to moderate absorption band ($\epsilon_{max} \sim 600$) at ~440 nm due to $n-\pi^*$ transition[3,6-7]. The later absorption is generally masked under the strong $\pi-\pi^*$ absorption in the azo dyes and related compounds[1-3,6-11]. Because of this all the functionally substituted azo compounds and their organotin derivatives so far studied show a single strong absorption band in the visible region except when solvent-solute interaction, e.g., *H*-bonding, solvation of the tin atom or solvent dependent azo-hydrazone tautomeric equilibria[3,12-16] etc., leads to the formation of new species which are characterised by new absorption bands in the spectrum.

The absorption maxima of the triorganotin-*o*-(4-N,N-dimethyl aminobenzene azo)benzoates (I), the corresponding methyl ester (II) and 4-N,N-dimethyl amino azo benzene (III) are given in Table 1.

TABLE 1—ABSORPTION MAXIMA (nm) IN THE SPECTRA OF THE AZO DYES AND THEIR ORGANOTIN DERIVATIVES

Solvent/Solute	IA	IB	II	III
Cyclohexane	405, 470[d]	395, 470[d]	400	398[a]
Carbon tetrachloride	405, 460[d]	410, 460[d]	401	—
Benzene	425[d], 480	420[d], 480	412	410
Acetone	420[d], 490	410, 490[d]	—	411[b]
Methanol	415, 490[d]	410, 488[d]	418	410[c]
DMSO	415	412	425	—
Pyridine	425	419	420	—

(a) iso-octane, (b) ethyl methyl ketone, (c) ethanol, (d) wave length corresponding to the shoulder/inflexion in the spectrum.



As expected, II and III show only a single absorption maximum at ~400-425 nm in all solvents. However, the spectra of the triorganotin derivatives (I) show solvent dependent absorption band in the range ~460-500 nm (except in pyridine and DMSO) in addition to the expected absorption in ~400-430 nm region in agreement with that of the closely similar compounds, II and III. Obviously, the ~400-430 nm absorption in I is due to $\pi-\pi^*$ transition in the azo part of the organotin complex (LE transition) while the solvent dependent ~460-500 nm absorption should be attributed to solvent-solute interactions. Since the intensity of the later band increases with a concomitant decrease in the intensity of the ~400-430 nm absorption, it also originates from the same $\pi-\pi^*$ transition which is modified by solvent-solute interaction, presumably through formation of solvent-solute complexes. Unfortunately, a direct quantitative estimation of the band intensities is not possible due to considerable overlapping of the two bands. To obviate this difficulty, the experimental absorption curves were fitted analytically by a linear combination of gaussian functions[17], each gaussion component in the final fit representing one absorption band (Appendix I). As expected from the nature of the absorption curves (Figs. 1 and 2) the experimental optical density data can be reproduced within the experimental errors by a single gaussian curve for pyridine or DMSO solutions, while a superposition of two gaussian curves is necessary for the spectra of I in other solvents. The band maxima, integrated molar absorptivity and the total

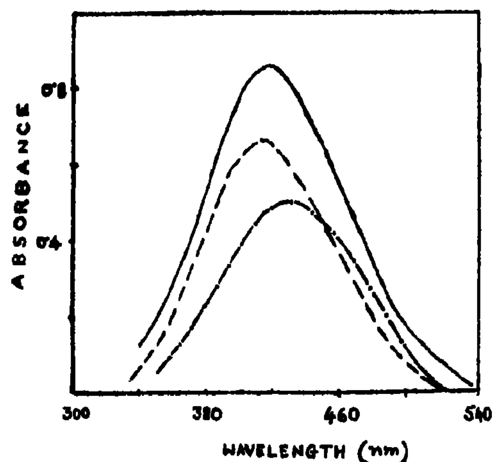


Fig. 1. Spectrum of IA (——), IB (- - - -) and II (— — —) in DMSO.

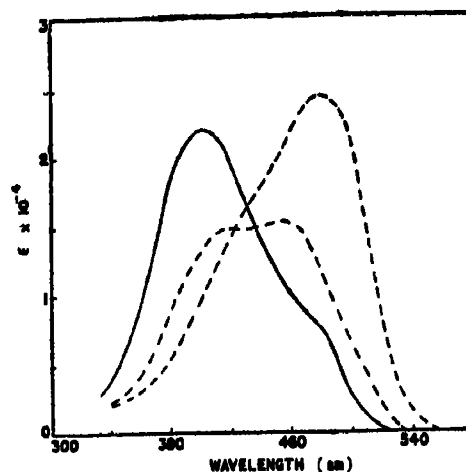


Fig. 2. Spectrum of IA in cyclohexane (——), benzene (- - - -) and carbon tetrachloride (— — —).

oscillator strength of the visible band system in different solvents are given in Table 2. The oscilla-

TABLE 2—SPECTRAL DATA ON THE VISIBLE BAND SYSTEM OF IA IN DIFFERENT SOLVENTS OBTAINED BY GAUSSIAN ANALYSIS

Solvent	Band 1		Band 2		Total oscillator strength
	λ_{max} (nm)	$A \times 10^{-7}$ (a)	λ_{max} (nm)	$A \times 10^{-7}$ (a)	
Cyclohexane	400	12 0	471	1.0	0.50
n-Heptane	402	11.5	466	1.1	0.54
iso-Octane	402	11.4	468	1.1	0.54
Carbon tetrachloride	402	6.0	462	4.1	0.44
m-Xylene	418	6.5	476	4.5	0.61
Toluene	415	7.2	478	6.2	0.58
Benzene	427	5 6	484	6.0	0.50
Methanol	410	6 8	482	8.1	0.64
Acetone	422	6.8	489	8.4	0.66
Nitrobenzene	448	4.5	508	9 6	0.61
DMSO	415	14.6	—	—	0.68
Pyridine	425	16.0	—	—	0 69

(a) Integrated molar absorptivity in sec^{-1} cm^{-1} litre $mole^{-1}$.

tor strengths are typical of the $\pi-\pi^*$ transition in the azo compounds[6] and agree closely with that of the methyl ester (II) which, unlike the organotin compounds, does not show any detectable specific solvent-solute interaction. Clearly the visible absorption in these compounds arises from a LE transition within the azo ligand.

Addition of a more polar solvent, e.g., CCl_4, nitrobenzene etc. to a solution of I in inert solvents like alkanes, increases the intensity of the longest wavelength band with a corresponding decrease in the intensity of the lower wavelength band (Fig. 3). The total integrated absorption of the visible band system, however, remains nearly constant (Table 3). Clearly, this indicates a reversible equilibrium of the type (1) through solvent(S)-solute(D)interaction in which the two absorption bands, viz., ~460-500 nm and ~400-430 nm bands, correspond,

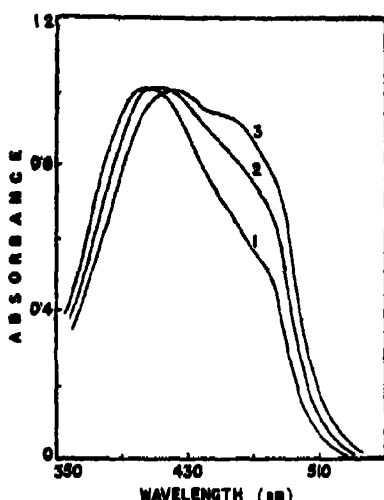


Fig. 3. Spectrum of IA in *n*-heptane containing (1) 20, (2) 60 and (3) 90% (v/v) CCl_4.

Table 3—Effect of CCl_4 and Nitrobenzene (A) on the Integrated Molar Absorptivities of π-π^* Transitions of IA and IB in Alkane

Solute/Solvent	A	Amount of A (% v/v) in solution	Integrated molar absorptivity $\times 10^{-7}$ Band 1	Band 2	Total
IA/*n*-hexane	nitrobenzene	0	11.96	1.02	12.98
		4	3.22	9.19	12.41
		10	2.41	9.80	12.21
		20	9.39	0.76	10.15
IA/*n*-heptane	CCl_4	60	9.04	1.27	10.31
		90	8.44	2.12	10.56
		100	5.97	4.13	10.10
IB/*n*-hexane	nitrobenzene	4	3.69	7.80	11.49
		8	2.60	9.97	12.57
		12	2.05	11.00	12.05
IB/*n*-heptane	CCl_4	5	12.34	0.75	13.09
		25	12.07	0.90	12.97
		70	11 91	1.10	13.01
		100	10.00	2.87	12.87

respectively, to the complexed and the uncomplexed species.



$$xD + yS \rightleftharpoons D_xS_y \quad .. \quad (1)$$

The approximate constancy of the total integrated absorptivity shows the oscillator strength of the $\pi-\pi^*$ transition in both the species to be the same. This is expected since the longest wave length absorption band in both the species arises from a slightly perturbed LE transition in the azo molecule bound to the triorganotin group through an ester linkage which is not conjugative. A simple perturbation treatment shows that the transition dipole, hence, the integrated absorptivity, of a LE transition in a weak molecular complex remains unchanged to the first order (Appendix II).

Stoichiometry and formation constants : Determination of the stoichiometry and the formation constant of a molecular complex generally requires the measurement of absorbance in a set of solutions in an inert or non-interacting solvent in which the concentration of one of the components is varied. The absorbance data can then be treated by one of the several methods available to determine the desired parameters. Although DMSO and pyridine apparently seems to be non-interacting in the present case (rather unusual !) in as much as the organotin compounds show only a single absorption band, these can not be used as a reference solvent because of their immiscibility with saturated hydrocarbons and due to the possibility of solvation of the tin atom which is well known in such system[8]. The following procedure was, therefore, adopted.

Consider 1 : 1 complex formation between a solute D and a reagent A in a solvent S which competes with A.



$$D + A \overset{K_{DA}}{\rightleftharpoons} DA \quad .. \quad (2)$$



$$D + S \overset{K_{DS}}{\rightleftharpoons} DS \quad (3)$$

Assuming the validity of Beer's law, the apparent molar absorptivity ϵ^λ, at a wavelength, λ, is given by

$$\epsilon^\lambda.C_D = \epsilon^\lambda_D[D] + \epsilon^\lambda_{DS}[DS] + \epsilon^\lambda_{DA}[DA] + \epsilon^\lambda_S[S] + \epsilon^\lambda_A[A] \quad . \quad (4)$$

where the symbol ϵ^λ_X denotes molar absorptivity of species X and the total concentration, C_D, of the solute is given by

$$C_D = [D] + [DA] + [DS] + \{1 + K_{DA}[A] + K_{DS}[S]\}[D] \quad ... \quad (5)$$

Since the measurements were done at a wavelength where the solvent and the reagent do not absorb and $[S] \gg C_D$; $[A] \gg C_D$, we obtain from eqns. (4) and (5)

$$\epsilon^\lambda = (\epsilon^\lambda_D + K_{DS}.\epsilon^\lambda_{DS}.C_S)/(1 + K_{DS}.C_S) + K_{DA}.C_A(\epsilon^\lambda_{DA} - \epsilon^\lambda)/(1 + K_{DS}.C_S) \quad .. \quad (6)$$

where C_S and C_A are the analytical concentrations of S and A respectively.

When the reagent A is a solid and used as a solution in the solvent, S, the solvent concentration remains constant and eqn. (6) can be reduced to the linear form

$$\epsilon^\lambda = \epsilon^\lambda_{DA} - (\epsilon^\lambda - \epsilon^\lambda_0)/(K'_{DA}.C_A) \quad . \quad (7)$$

where the apparent formation constant, K'_{DA}, is given by

$$K'_{DA} = K_{DA}/(1 + K_{DS}.C_S) \quad . \quad (8)$$

and ϵ^λ_0, the apparent molar absorptivity of the solute in the solvent S is given by

$$\epsilon^\lambda_0 = (\epsilon^\lambda_D + K_{DS}.\epsilon^\lambda_{DS}.C_S)/(1 + K_{DS}.C_S) \quad (9)$$

Since ϵ^λ and ϵ^λ_0 can be obtained from absorbance data, plot of $(\epsilon^\lambda - \epsilon^\lambda_0)/C_A$ vs ϵ^λ may be used to test the formation of 1 : 1 complex. However, the situation is more complicated in our case since the reagent A being a liquid, e.g., CCl_4, C_6H_6 etc., any increase in C_A results in concomitant decrease of C_S. Neglecting any change in volume due to mixing, it can be shown that

$$C_S = C^0_S - a_{SA}.C_A \quad ... \quad (10)$$

where C_S^0 is concentration of the pure solvent and

$$a_{SA} = M_A.\rho_S/(M_S.\rho_A)$$

where M_A, ρ_A and M_S, ρ_S are the molecular weight and density of A and S respectively.

Using eqn. (10), eqn. (6) can be reduced to the form

$$\epsilon^{\lambda} = \epsilon - (\epsilon^{\lambda} - \epsilon_0^{\lambda})/K.C_A \quad . \quad (11)$$

where $\epsilon = (K_{DA}.\epsilon_{DA}^{\lambda} + K_{DS}.a_{SA}.\epsilon_D^{\lambda})/(1 + K_{DS}.C_S^0)$ ... (12)

and $K = (K_{DA} - K_{DS}.a_{SA})/(1 + K_{DS}.C_S^0)$ ... (13)

Since C_D is usually kept fixed while C_A is systematically varied, one may use the optical densities, d^{λ}, instead of the molar absorptivities and plot $(d^{\lambda} - d_0^{\lambda})/C_A$ vs d^{λ} to test the presence of 1 : 1 complex forming equilibria. A few typical plots for IA using a hydrocarbon as reference solvent are shown in Figs. 4 and 5. The linearity of the plots

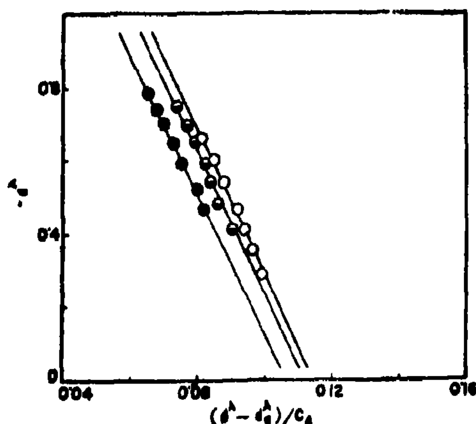


Fig. 4. Plot of d^{λ} vs $(d^{\lambda} - d_0^{\lambda})/C_A$ for IA in cyclohexane containing 5-35% (v/v) benzene at 470 nm (–●–●–), 480 nm (–◐–◐–) and 490 nm (–○–○–).

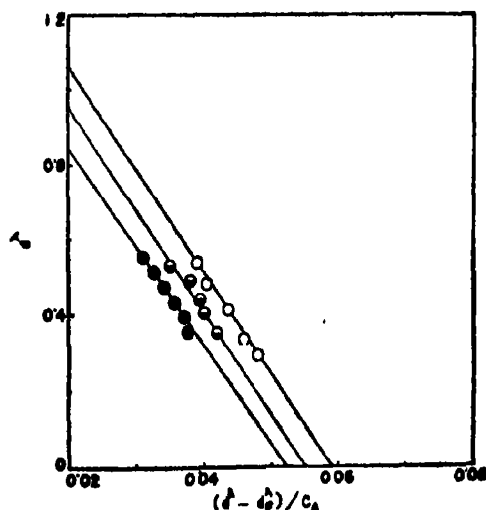


Fig. 5. Plot of d^{λ} vs $(d^{\lambda} - d_0^{\lambda})/C_A$ for IA in cyclohexane containing 10-60% (v/v) toluene at 470 nm (–●–●–), 480 nm (–◐–◐–) and 490 nm (–○–○–).

and the constancy of the slopes at different wavelengths confirm the formation of 1 : 1 complexes by the organotin compounds. The experimental conditions and the apparent formation constants obtained from the plots are given in Table 4.

TABLE 4—EXPERIMENTAL CONDITIONS AND THE APPARENT FORMATION CONSTANTS FOR SOME IA-S-A SYSTEMS

S	A	$C_D \times 10^5$ (M)	Range of C_A (M)	$K \times 10^{2(a)}$ (litre mole^{-1})
Cyclohexane	Nitrobenzene	2.752	0.97-5.84	9.9
Cyclohexane	Benzene	4.876	0.56-3.94	5.1
Cyclohexane	Toluene	2.898	0.94-5.64	3.7
Cyclohexane	m-Xylene	3.213	0.81-4.86	3.8
n-Pentane	Benzene	4.876	0.56-3.94	6.8
		2.436	1.12-6.76	6.2
n-Hexane	Benzene	6.932	0.56-3.94	6.0
n-Heptane	Benzene	4.876	0.56-3.94	7.2
		2.208	1.12-6.76	7.4
i-Octane	Benzene	3.569	1.12-6.76	6.7
		2.187	1.12-6.76	6.9
n-Heptane	CCl_4	5.511	1.03-7.24	5.1
CCl_4	Chloranil	5.511	$0.44-1.62 \times 10^{-2}$	8.2×10^4

(a) Average of the values calculated from the plots of data at three different wave lengths.

Though the linearity of the plots and the constancy of the calculated values of K confirm the formation of molecular complexes and its stoichiometry, the evaluation of the true formation constants require the use of a truly inert solvent ($K_{DS}=0$) which is, unfortunately, not feasible experimentally in our case. To overcome this difficulty we therefore used a more direct approach based on the constancy of the integrated absorptivity of a LE transition in a weak complex which, in our case, is confirmed experimentally (Table 3) as well as theoretically (Appendix II).

Since the integrated molar absorptivities of the $\pi - \pi^*$ transition in the complexed and the uncomplexed species are the same, the areas under the corresponding absorption bands, i.e., the integrated absorbances, A_{DA} and A_D are proportional to the concentrations of the species DA and D respectively. Thus,

$$K_{DA} = [DA]/([D].[A]) \simeq A_{DA}/(A_D.C_A) \quad ... \quad (14)$$

because $[A] \simeq C_A$ since $[D] \ll C_A$.

Using the integrated absorbances of the two bands obtained through a gaussian analysis (Appendix I) of the absorption curves in a given solvent, the formation constants were calculated through eqn. (14). The values are given in Table 5. A comparison of the values given in Tables 4 and 5 shows the apparent formation constants to be lower, even when the reference solvent is a saturated hydrocarbon which are considered to be inert solvents, than the formation constants determined through eqn. (14). Eqn. (13) which relates the apparent formation constant with the true formation constant, and the formation constant of the solvent-solute

TABLE 5—FORMATION CONSTANTS OF COMPLEXES OF I WITH DIFFERENT MOLECULES (A)

A	$K_{DA} \times 10^2$ (litre $mole^{-1}$) IA	IB	IC
Chloranil	1.89×10^4	8.0×10^4	
Nitrobenzene	21.8	17.9	
Benzene	9.2	4.9	6.2
Toluene	9.0		
Acetone	9.0	2.2	
m-Xylene	8 6		
Carbon tetrachloride	6.7	2.6	
Acetonitrile	6.2		
i-Octane	1.6	0.88	1.4
n-Heptane	1.5	0.98	1.7
n-Pentane	1.1	0 72	
n-Hexane	0.98	0.56	1.9
Cyclohexane	0.92	0.86	

complex, K_{DS}, then requires K_{DS} to be finite even in hydrocarbon solvents. For example, inserting the values of appropriate formation constants from Tables 4 and 5 in eqn. (13), a value of ~0.02 litre/mole is obtained for the IA-cyclohexane complex, the value obtained by direct method being ~0.01 litre/mole. In view of the large uncertainties associated with the parameters obtained through the use of eqn. (11), the agreement is quite satisfactory. Because of the low values of the formation constants a knowledge of the errors involved and the reliability of the calculated values are crucial in deciding whether or not the complexes should be regarded as collision or contact complexes. This point is examined in Appendix III.

Nature of the complexes: Since the solvent-solute interaction with the organotin compounds, I, takes place even in non polar and aprotic solvents, H-bonding and solvation of the tin atom through coordination can be ruled out. The increase in the value of K_{DA} for a given organotin compound (D) with different A in the sequence: A = alkane < CCl_4 < xylene ~ toluene ~ benzene < nitrobenzene ≪ chloranil suggests a correlation with the acceptor strength of A. Again, the spectrum of I-nitrobenzene system in n-hexane shows a new absorption band at ~376-388 nm inaddition to the ~490 nm $\pi-\pi^*$ transition of the complexed species (Fig.6). This band may be reasonably assigned to a charge-transfer (CT) transition of the I-nitrobenzene complex. The bathochromic shift and the increase in its intensity with nitrobenzene concentration which increases the solvent polarity and thereby stabilizes the more polar CT state relative to the ground state, supports this assignment. The complexes are, presumably, of donor-acceptor type in which the organotin molecule acts as the donor. However, no such CT band is found with other reagents. This is not surprising because the CT transition is expected to occur at much lower wavelength with benzene, toluene etc. and may be completely masked under their absorption bands. In case of I-alkane complexes, the CT state will definitely lie very much above the ground state due to the nonavailability of any low lying acceptor orbitals in alkanes thereby making it inaccessible.

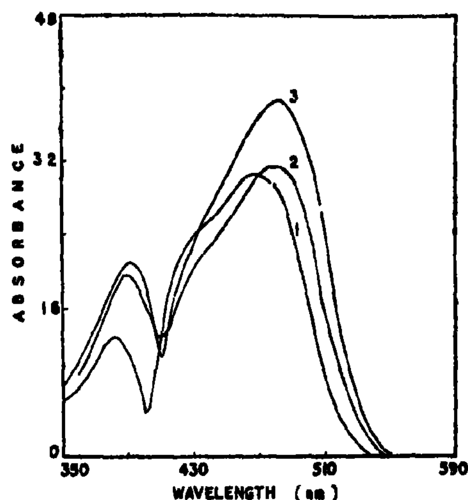


Fig. 6. Spectrum of IA in n-hexane containing (1) 4, (2) 10 and (3) 15% (v/v) nitrobenzene.

On the other hand, the complexes, atleast in some cases, may be formed through Van der Waals or dipole-dipole interactions which play important role in many weak complexes[18-25]. However, the bathochromic shift of the π-π^* transition on complexation suggests a significant contribution from the polar structure $D^{\delta+}A^{\delta-}$ because the lowering of the π^*-level in azo dyes is generally indicative of lowering of electron density in the molecule[6]. For example, the protonated species, formed in acid medium, show a bathochromic shift of ~50-100 nm in most cases[9-11,26-29].

The small values of the formation constants (K<0 1) are often regarded as an indication of collision or CCT (contact charge transfer) complexes[30]. Murrell[31], on the other hand, has shown such distinction to be wholly unnecessary when the solvation is taken into account. In fact, the concept of CCT in solution is nebulous when it is based on the magnitude of the formation constant only[30,42]. The existence of a chemically distinguishable species in the present case can be convincingly demonstrated by the effect of protic solvents, e.g., methanol. For example, the addition of methanol to a solution of I in any other aprotic solvent brings about the following changes in its spectrum: (i) a new absorption band appears with concomitant decrease in the intensity of original absorption bands due to the complexed (DA) and uncomplexed species (D). The position of the new band depends only on the organotin molecule, D (Table 6) (ii) at high methanol concentration (>30% v/v) all the curves pass through an isobestic point (Fig. 7) and (iii) the intensity of the new absorption reversibly increases with decrease of pH showing this to be associated with the protonated species (Fig. 7).

A quantitative study of the effect of pH on the organotin compounds in H_2O-methanol mixtures of

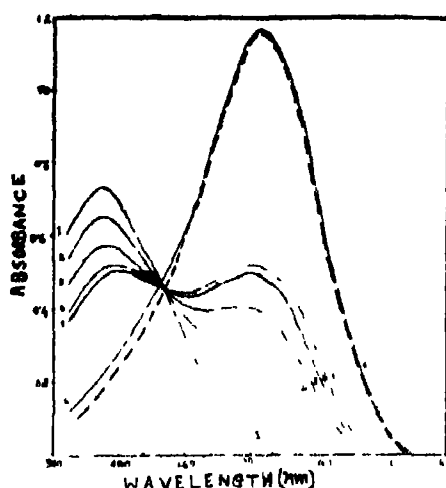


Fig. 7. Spectrum of IC in pure methanol (2) and in presence of 80%(v/v) n-C_6H_{14}(3), CCl_4(4), C_6H_6(5), Chloranil(6), 2 equiv. HCl (— — —), NH_4OH(1).

Table 6—Position of the Longest Wavelength Band in Some D-A-MeOH Systems

Compound	IA	IB	IC
λ_{max} (nm)	492	488	508

different compositions confirms the presence of the equilibrium :



$$D + H^+ \overset{K_b}{\rightleftharpoons} DH^+ \quad (15)$$

Assuming the validity of Beer's law, it is possible to deduce the following relation for this equilibrium

$$\epsilon^\lambda = \epsilon^\lambda_{DH+} - (\epsilon^\lambda - \epsilon^\lambda_D).\ \ 10^{-pH}/K^b \quad (16)$$

were ϵ^λ, ϵ^λ_{DH+} and ϵ^λ_D are respectively, the molar extinction of the solution, DH^+ and D at the wavelength, λ.

Experimental verification of the Beer's law and eqn. (16) both confirm the formation of DH^+ and yields the value of the basicity constant, K_b. The pK_b values of the relevant azo compounds in 100% methanol obtained by extrapolation are given in Table 7.

Table 7—pK_b in Pure Methanol of Some Azo Dyes and their Organotin Derivatives

Compound	pK_b
IA	−6.27
IB	−6 10
II	−2.60
IV	−8.10
o-(4-N,N-dimethyl amino benzene azo)-benzoic acid	−5.90
Azobenzene	−2.90[a]
4-N,N-dimethyl amino azo benzene	−3.50[b]

(a) Ref. 11, (b) Ref. 26.

Interestingly, the same protonated species, as shown by the absorption spectrum as well as the effect of pH, is formed by the addition of an alkane, CCl_4, ether, benzene etc. or an acceptor like chloranil, DDQ etc. The increase in $[DH^+]$ with increase in [A] in methanol, even when A is an alkane (Fig. 8) can be explained only through the formation of a species involving D and A which is

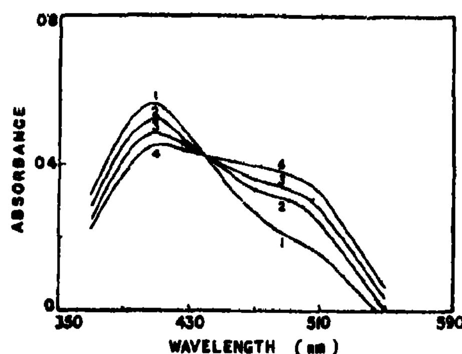
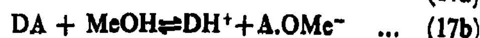


Fig 8 Spectrum of IA in (1) pure methanol and in presence of (2) 10, (3) 20 and (4) 40% (v/v) cyclohexane in methanol.

then solvolysed by the protic solvent as shown below.



$$D + A \rightleftharpoons DA \quad (17a)$$



$$DA + MeOH \rightleftharpoons DH^+ + A.OMe^- \quad (17b)$$



$$DH^+ \rightleftharpoons D + H^+ \quad (17c)$$

Although the formation of $A.OMe^-$ in eqn. (17b) has been invoked to balance it, evidence for this species has now been obtained when A is a strong acceptor e.g., chloranil. The difference spectrum of D-chloranil-MeOH system and D-DH^+ system (obtained by addition of dil. HCl to methanolic solution of D till the absorption due to DH^+ becomes identical in both the systems) shows an absorption at ~420 nm which is absent in the spectrum of chloranil in the same solvent (Fig. 9). Since the difference spectrum is independent of the nature of D, it is associated only with the chloranil containing species. A similar absorption is found in the spectrum of chloranil in presence of Na-methoxide and is, presumably, due to [chloranil − OMe^-] complex since many anions are known to form CT complexes with chloranil[29-31].

The effect of methanol thus strongly supports the formation of molecular complexes by the organotin compounds of type I with all types of molecules including the alkanes, albeit, very weak. Preliminary studies on the effect of temperature on this system showed no detectable change in the optical density for a ~10° change in temperature. The maximum error involved in K which is ~6% (Appendix III) then puts an upper limit of 1 Kcal/mole to the heat of formation. Such a small stabilization of the ground state coupled with a

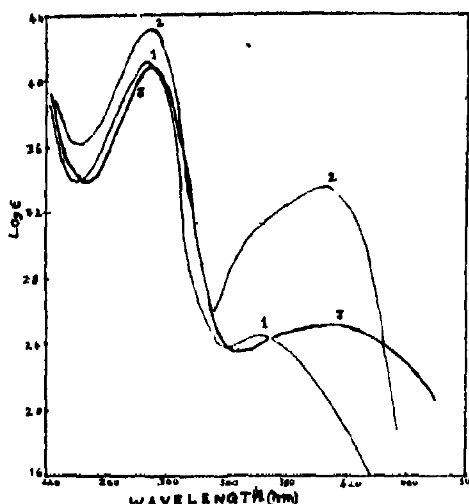
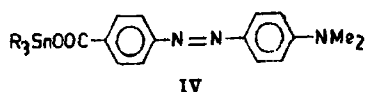
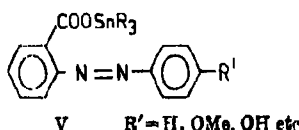


Fig. 9 Spectrum of chloranil in methanol (1), the difference spectrum of D-chloranil-MeOH system (2) and spectrum of chloranil in methanol containing 1 equiv. NaOMe (3).

considerable bathochromic shift of the π-π^* transition therefore suggests greater stabilization of the excited state on complexation.

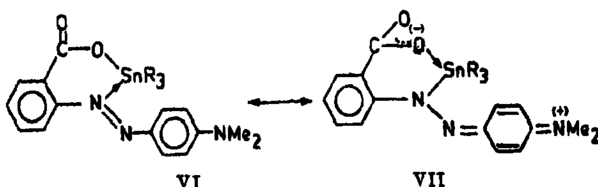
Structure and donor properties of the organotin compounds · The unusual donor ability is lost in *p*-carboxy compounds (IV) or in compounds in which the amino group is replaced by other groups (V).





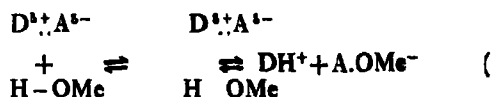
V R' = H, OMe, OH etc

The loss of donor ability of I in pyridine and DMSO in which 5-coordinate organotin-*o*-(aryl azo)-benzoates undergo facile solvolysis through cleavage of the chelate ring as well as in the *p*-carboxy compound, V, where no chelate ring is present in contrast to the *o*-carboxy compound (VI)[1,2], shows this ring to be essential for the unusual donor ability.



This is probably due to the resonating structure VII which makes the –COO group electron rich in such molecules resulting in high donor ability. The importance of structure VII is shown by the relatively low asymmetric OCO stretch in s compounds (~1600 cm^{-1})[1]. The high polarity the Sn–O bond, estimated to be ~51% fi Pauling's electronegativities[a], enhances the elect density on the –COO group. The fact that c highly basic molecules (pK_b ~ –6.0, see Table 7) able to show such unusual donor ability suppo this. Since the structure VII is certain to m greater contribution to the excited state than ground state, the excited state is expected to more stabilized on complexation in agreement w the observed bathochromic shift of the π transition.

The formation of DH^+ by the action methanol on the molecular complexes (DA) can explained by the initial formation of H-bond w the O-atom of the –COO group which atta higher effective electronegativity in the comp due to partial removal of electron density from to A, followed by a rearrangement to the fi species as shown below.



While much work remains to be done before t unusual donor ability of the organotin compoun of type I can be fully understood and explored, t present investigations open up the possibility preparing complexes of saturated hydrocarbo which was highlighted by Prof. Chatt in his lectu "25 years of the ICCC : Prospect and Retrospect"

Acknowledgement

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Appendix I

Resolution of absorption curves :

The absorption curves were represented by analytical function of the type :

$$A_\nu = \sum A^k_{max} \text{Exp}\left[-b\left\{\left(\nu - \nu^k_{max}\right)/\Delta\nu^k_{1/2}\right\}^2\right] \quad .. \quad (A1)$$

where A_ν is the absorbance at frequency ν ; ν^k_{max}, A^k_{max} and $\Delta\nu^k_{1/2}$ are, respectively, the position of the maximum, absorbance at the maximum and halfwidth of the k th band ; b is a constant. The oscillator strength, f, of the band system is given by

$$f = 4.32 \times 10^{-9}\int_{band} A_\nu . d\nu = 4.60 \times 10^{-9} \sum_k A^k_{max} . \Delta\nu^k_{1/2} \quad .. \quad (A2)$$

The experimental curves were fitted by an iterative process in which the parameters A^k_{max}, ν^k_{max} and $\Delta\nu^k_{1/2}$ were varied till the error was minimized (least square technique)[17].

Appendix II

Transition moment of a LE transition in a weak molecular complex :

Consider a LE transition $\psi_{k(D)} \to \psi_{l(D)}$ in the component, D, of a weak molecular complex, DA. Using perturbation theory[6,38], we have

$$\psi_{k(D)} = \psi^0_{k(D)} + \lambda \sum_{i(\neq k)} \frac{\langle \psi^0_{k(D)} | h' | \psi^0_{i(A)} \rangle}{E^0_k - E^0_i} \psi^0_{i(A)} + \quad .. \quad (A3)$$

where $\psi^0_{k(D)}$ and $\psi^0_{i(A)}$'s are the MO's of the separated components D and A respectively and $\lambda h'$ is the perturbation due to complexation, λ being the perturbation parameter[38].

In a weak complex, perturbation being small, terms higher than the first order can be neglected. The transition moment is therefore given by

$$\langle \psi_{k(D)} | \mu | \psi_{l(D)} \rangle = \langle \psi^0_{k(D)} | \mu | \psi^0_{l(D)} \rangle + \left[\sum_{i(\neq k)} \frac{\langle \psi^0_{k(D)} | h' | \psi^0_{i(A)} \rangle \langle \psi^0_{i(A)} | \mu | \psi^0_{l(D)} \rangle}{E^0_k - E^0_i} \quad .. \quad (A4)$$
$$+ \sum_{i(\neq l)} \frac{\langle \psi^0_{l(D)} | h' | \psi^0_{i(A)} \rangle \langle \psi^0_{k(D)} | \mu | \psi^0_{i(A)} \rangle}{E^0_l - E^0_i} \right]$$

Since $\psi^0_{k(D)}$ and $\psi^0_{l(D)}$ are localized on D while $\psi^0_{i(A)}$'s are localized on A, all matrix elements between these vanish in ZDO approximation which is correct to first order in overlap[43]. Hence,

$$\langle \psi_{k(D)} | \mu | \psi_{l(D)} \rangle \simeq \langle \psi^0_{k(D)} | \mu | \psi^0_{l(D)} \rangle \quad ... \quad (A5)$$

showing the transition moment of a LE transition remains unchanged, to a good approximation, on complexation.

Appendix III

Relative error in the estimation of formation constants :

For a gaussian curve

$$A_\nu = A_{max}.\text{Exp}[-a(\nu - \nu_{max})^2] \quad ... \quad (A6)$$

the integrated absorbance, A, is given by

$$A = \int_{band} A_\nu . d\nu = \sqrt{\pi/a}. A_{max} \quad .. \quad (A7)$$

The relative error, $\Delta A/A$, is then obtained by differentiation,

$$\Delta A/A = (\Delta A_{max}/A_{max} - \Delta a/2a) \quad .. \quad (A8)$$

Analysis of the absorbance data calculated from gaussian functions (A6) shows the maximum error in A_{max} and a obtained from least square fit to be $\pm 2\%$ giving a maximum limit of $\pm 3\%$ error in the integrated absorbance data. Therefore, the relative error in the formation constants calculated by the use of eqn. (14) is given by

$$\Delta K_{DA}/K_{DA} = |\Delta A_D/A_{DA}| + |\Delta A_D/A_D| \doteq 6\%$$

Unlike the Benesi-Hildebrand equation[39] or its variants[40,41] where linearization is achieved through variables which often involve reciprocal of optical densities so that large errors frequently creep into the estimated values of K and ϵ_{max}, particularly for K <0.1, making the results suspect, the present method is free from such sources of errors so that the estimated values of K_{DA} can be used with confidence.

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Copolymerization of Acrylonitrile with [(2-Methacryloyloxy)alkoxy]trimethyl Silanes

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Acrylonitrile (AN) was copolymerized with [(2-methacryloyloxy)ethoxy]trimethylsilane (2-MAETMS) and [(2-methacryloyloxy)propoxy]trimethylsilane (2-MAPTMS) in dimethylformamide and dimethylsulfoxide at temperatures between 50° and 70° using azobisisobutyronitrile(AIBN) as initiator The copolymer composition was determined by silicon estimation and reactivity ratios were calculated by the Kelen-Tudos method. In both the systems, r_1(AN) and r_2(2-MAETMS/2-MAPTMS) are higher in DMF compared to the values in DMSO. Arrhenius parameters were derived for AN-2-MAETMS system. The difference between the activation energies ($E_{12}-E_{11}$) favour self-propagation for the acrylonitrile radical, whereas A_{11}/A_{12} favours cross-propagation. In case of 2-MAETMS radical, $E_{22}-E_{21}$ favours cross-propagation but A_{22}/A_{21} favours self-propagation. The influence of the comonomers on some of the basic properties of copolymers like solubility, intrinsic viscosity, softening and glass transitions have also been studied.

COPOLYMERIZATION of acrylonitrile with various allyl and vinylsilanes e.g., allyltrimethylsilane, dimethylphenyl vinylsilane, methyl vinyl diethoxysilane and vinyltrimethylsilane has been investigated[1-5]. Poor reactivity of vinylsilanes in copolymerization of styrene with vinyltriethoxy, vinyltriacetoxysilane and vinylmethyldiacetoxysilane[6,7] has been observed by us.

In addition, the effect of silane monomers, e.g on copolymerization of styrene with [(2-methacryloyloxy)ethoxy]-trimethylsilane, 2-MAETMS (in which silicon atom is not in the vicinity of vinyl double bond) has been reported previously[8]. The studies have now been extended to the copolymerization of acrylonitrile (M_1) with 2-MAETMS and 2-MAPTMS (M_2) to determine the effect of substituent, solvent medium and the polymerization temperature on the monomer reactivity ratios

Experimental

Acrylonitrile (BDH) was dried over fused calcium chloride after making it free from the inhibitor and distilled before use under nitrogen at 77°. DMF was dried over calcium oxide and distilled at 152°. Dimethylsulfoxide (DMSO) was distilled at 95°/20 mm Hg and kept under nitrogen atmosphere.

2-MAETMS and 2-MAPTMS were prepared from 2-hydroxyethylmethacrylate (2-HEMA) or 2-hydroxypropylmethacrylate (2-HPMA) and trimethylchlorosilane in the presence of triethylamine following the method of Antiopina *et al*[9]. 2-MAETMS was distilled at 71-72°/2 mm Hg and 2-MAPTMS at 78-80°/2 mm Hg.

The copolymerization of acrylonitrile with 2-MAETMS or 2-MAPTMS was performed in DMF or DMSO in inert atmosphere in the temperature range 50-70°. AIBN (1 mole % on the basis of total monomers) was used as initiator and the total concentration of monomers amounted to 4 moles/litre. The time necessary for high conversions was found from time vs conversion plots. The products were isolated by precipitation in methanol and purified by repeated dissolution and precipitation. The polymers were then dried at 50° under vacuum to constant weight. The composition of copolymers was determined from silicon contents estimated gravimetrically.

The infrared spectra of the copolymers were recorded in potassium bromide between 700-4000 cm^{-1} on Grubb Parson spectrophotomer. For determination of copolymer composition, 2.5% of polyacrylonitrile or its copolymers in KBr were prepared and their spectra were recorded. The peak height for the nitrile group at 2260 cm^{-1} was measured. Considering peak height in case of polyacrylonitrile equivalent to 100 parts of acrylonitrile, corresponding acrylonitrile contents were calculated for AN-2-MAETMS copolymer by the following procedure[11].

Let A = percent of AN moiety in copolymer and B = 100-A = percent of comonomer moiety in copolymer. Then number of moles of AN in 100 gm copolymer $=\frac{A}{53}=X$, and number of moles of comonomer in 100 g copolymer $=\frac{B}{M}=Y$, where M is molecular weight of silylated comonomers used in our studies. Mole fraction of acrylonitrile moiety in the copolymer $=\frac{X}{X+Y}$

The proton magnetic resonance spectra of the polymers were recorded on a 90 MHz Varian spectrophotometer. 5% (v/v) solution of the

polymer was made in trifluoroacetic acid. Tetramethylsilane was used as internal standard.

The intrinsic viscosity was determined in DMF at 30° using Ubbelohde suspension level viscometer.

The softening ranges were measured in capillaries with a temperature rise of about 5°/min.

The solubility of the acrylonitrile copolymers was checked in DMF, DMSO and toluene at 30°.

The glass transition temperatures of polymers were determined with a Perkin-Elmer model DSC-2 differential scanning calorimeter. The polymer samples, weighing 10 mg each, were placed in standard DSC aluminium pans. Empty aluminium pan was used on the reference side of the instrument. Both sample and reference pans were enclosed with aluminium covers and sealed with the special press designed for the purpose. The pans were then placed in the cell compartments of the DSC instrument, where a continuous stream of pure dry helium is made to flow at a rate of 20 cm^3/min. In order to have a homogeneous polymer sample it was heated for few seconds to a temperature 30° above the T_g estimated from a preliminary run. After homogenising, the sample was quenched through the glass transition region at a rate of 320°/min as suggested in the literature[12]. After quenching, T_g values of the polymer sample were determined by heating these at a rate of 20°/min, chart speed 20 mm/min and setting of range control 2 mcal/sec. For quantitative analysis, following settings were used on DSC-2 instrument . rate of heating 20°/min, chart speed : 20 mm/min and sensitivity range 5 mcal/sec. Enthalpy of nitrile group polymerization which occurs in the range 290-340 in copolymers (as an exothermic peak) was calculated from DSC thermograms using the following expression as given in Perkin Elmer handbook[13].

$$\Delta H = \frac{K.R.A.}{W.C_S}$$

were, ΔH=heat of nitrile group polymerization ; W=weight of sample in mg ; C_S=chart speed in cm/sec ; A=area under the curve in cm^2 and K= instrument constant computed from the following expression and its value found to be 1.46.

$$K = \frac{\Delta H_f \cdot W_{std} \cdot S_{std}}{R.A.}$$

ΔH_f=heat of fusion of Indium (calibrating standard) in mcal/mg ; W_{std}=weight of calibrating standard in mg ; S_{std}=chart speed in cm/sec for the standard run ; R=setting of range control in mcal/sec (full scale) divided by chart span in cm to yield in mcal/sec cm and A=area under curve for calibrating standard in cm^2. ΔH_f of Indium was found to be 6.8 cal/g.

Results and Discussion

Polymerization of acrylonitrile and its copolymerzation with 2-MAETMS and 2-MAPTMS was carried out at 60° in DMF for different intervals of time. It has been observed that the rate of copolymerization is higher than that of homopolymerization of acrylonitrile (Fig. 1), which may be related to the higher reactivity of silane comonomers. In addition, the slow rate of homopolymerization of acrylonitrile may be attributed to side reactions of polyacrylonitrile radical. Patron and others[13,14] suggested that polyacrylonitrile radical undergoes

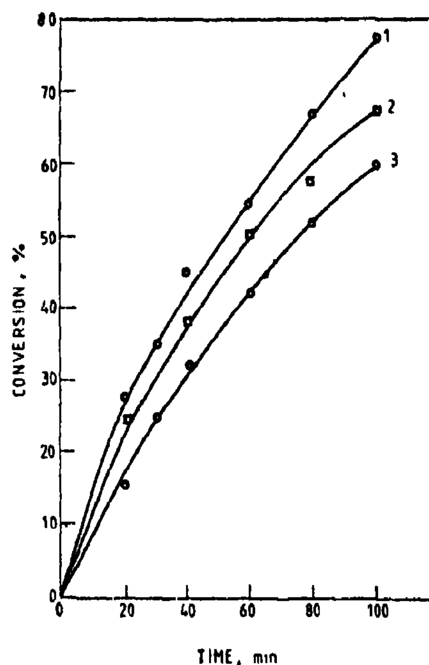
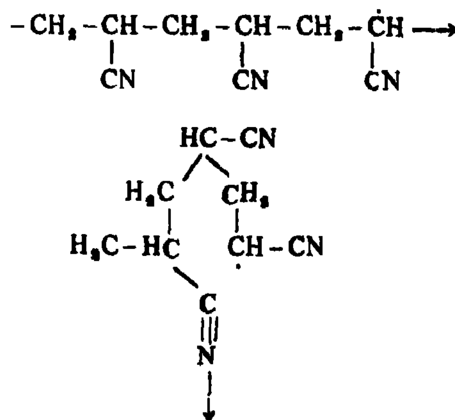
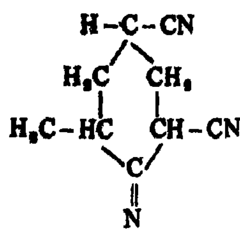


Fig. 1. Time vs conversion plot for polymerization of (1) AN-2-MAETMS (2) AN 2-MAPTMS (3) AN at 60° in DMF

cyclization or oligomerization in DMF forming cyclic imine radical leading to low reactivity in propagation reactions which results into both, decrease of reaction rate and molecular weight. Due to bulky side substituents in silylated comonomers, 2-MAETMS and 2-MAPTMS, cyclization will be to a lesser degree thereby leading to higher copolymerization rate. Further, the copolymerization





rate for P(AN-2-MAPTMS) is lower than P(AN-2-MAETMS) due to increased size of side substituents in 2-MAPTMS,



It is also interesting to note that no autoacceleration occurs in solution copolymerization of acrylonitrile as observed in bulk polymerization of acrylonitrile by Bamford and Jenkins[14].

Results of copolymerization of acrylonitrile with 2-MAETMS and 2-MAPTMS are shown in Tables 1 and 2. Copolymer composition vs composition of monomer feed plot (Fig. 2) indicates that copolymers have low acrylonitrile content than the monomer feed. At the same feed ratio however, the copolymers have higher acrylonitrile (m_1) content in DMF solutions as compared to polymers prepared in DMSO. This may be due to the higher reactivity of polyacrylonitrile radical in DMF which is a solvent with about the same polarity and dielectric constant (AN, $\epsilon = 38$, DMF, $\epsilon = 35$). From these copolymer compositions data, reactivity ratios

TABLE 1—COPOLYMERIZATION OF ACRYLONITRILE (M_1) WITH 2-MAETMS (M_2)

Medium	M_1 mole fraction in feed	Conversion %	Copolymer composition: silicon content %	Copolymer composition: M_1 mole fraction	[η] dlg⁻¹
			50°		
DMF	0.92	22.8	5.78	0.845	0.39
	0.90	25.2	6.42	0.816	0.46
	0.875	21.8	7.44	0.768	0.49
	0.80	19.9	8.65	0.685	0.55
			60°		
	0.92	31.6	6.55	0.810	0.41
	0.90	30.4	7.36	0.772	0.44
	0.875	28.1	8.28	0.724	0.51
	0.80	30.1	9.58	0.632	0.56
			70°		
	0.92	33.9	7.59	0.760	0.49
	0.90	32.5	8.51	0.707	0.58
	0.875	30.8	9.39	0.648	0.56
	0.80	27.7	10.39	0.568	0.59
			60°		
DMSO	0.92	28.7	6.90	0.795	0.42
	0.90	26.1	7.71	0.754	0.48
	0.875	26.8	8.48	0.709	0.51
	0.80	27.1	9.55	0.628	0.56

[η] Intrinsic viscosity at 30° in DMF.

TABLE 2—COPOLYMERIZATION OF ACRYLONITRILE (M_1) WITH 2-MAPTMS (M_2) AT 60°

Medium	M_1 mole fraction in feed	Conversion %	Copolymer composition: silicon content %	Copolymer composition: M_1 mole fraction	[η] dlg⁻¹
DMF	0.92	29.5	4.98	0.868	0.33
	0.90	26.5	6.07	0.828	0.36
	0.875	25.1	6.76	0.790	0.40
	0.80	25.3	8.20	0.705	0.42
DMSO	0.92	29.9	6.54	0.801	0.37
	0.90	26.4	7.62	0.742	0.41
	0.875	28.4	7.91	0.724	0.48
	0.80	24.5	9.23	0.625	0.49

[η] Intrinsic viscosity at 30° in DMF.

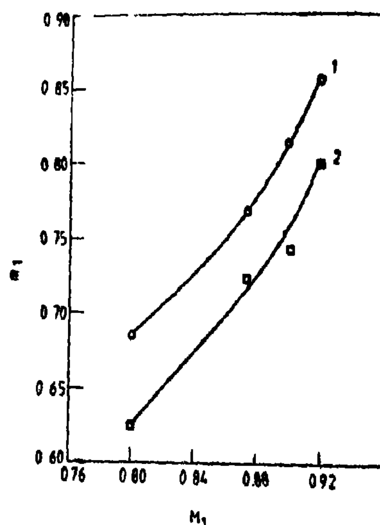


Fig. 2. Initial copolymer composition vs composition of monomer feed
(1) AN-2-MAPTMS in DMF
(2) AN-2-MAPTMS in DMSO

were calculated according to Kelen-Tudos method[15] represented by equation (ii).

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad \text{(ii)}$$

By plotting η value calculated from the experimental data as a function of ξ, a straight line is obtained, which on extrapolation to $\xi = 0$, and $\xi = 1$ gives corresponding $-\frac{r_2}{\alpha}$ and r_1 respectively both as intercepts. Advantages of this method over the conventional intersection and Fineman-Ross method have already been emphasized and its applicability for high conversion data has been reported[17]. Kelen-Tudos plots for AN-2-MAETMS and AN-2-MAPTMS systems in DMF and DMSO are given in Figs. 3 and 4 and values of r_1 and r_2 (Tables 3,4) were calculated from the data by linear least square

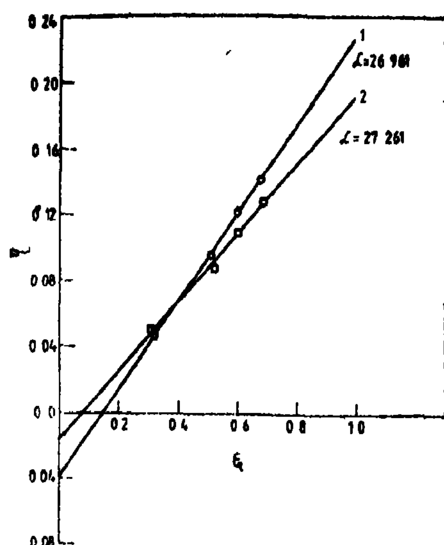


Fig. 3. Kelen-Tudos plot for copolymerization of AN-2-MAETMS at 60° in
(1) DMF, r_1=0.229 and r_2=1.018
(2) DMSO, r_1=0.198 and r_2=0.468

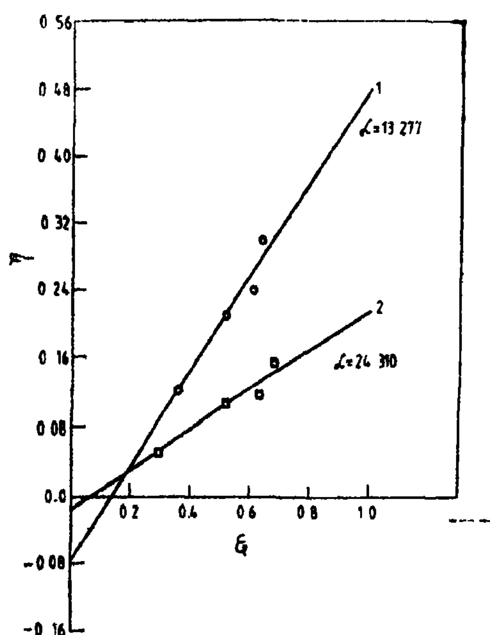


Fig. 4. Kelen-Tudos plot for AN-2-MAPTMS copolymerisation at 60° in
(1) DMF, r_1=0.485 and r_2=1.157
(2) DMSO, r_1=0.216 and r_2=0.894

method. The reactivity ratios in DMF at 60° are given below:

AN-2-MAETMS copolymer system,
r_1=0.229, r_2=1.018

AN-2-MAPTMS copolymer system,
r_1=0.485, r_2=1.157

The reciprocal of r_1 (AN) in both the systems viz., AN-2-MAETMS ($1/r_1$=4.37) and AN-2-MAPTMS ($1/r_1$=2.06) in DMF indicates the higher reactivity of 2-MAETMS compared with 2-MAPTMS towards polyacrylonitrile radical. Moreover, $1/r_1$(AN) values of AN-HEMA and AN-HPMA systems[10] are 37.04 and 27.78 respectively implying higher reactivity of hydroxyalkylacrylates in comparison to their silylated derivatives i.e., 2-MAETMS and 2-MAPTMS.

Effect of solvents on reactivity ratios : A perusal of the reactivity ratios in DMF and DMSO (Table 3) reveals that both r_1(AN) and r_2(2-MAETMS or 2-MAPTMS) are higher in DMF compared to the values in DMSO. A change in r_1(AN) value due to solvents means a change in the ratio k_{11}/k_{12} where k_{11} and k_{12} are the rate constants for the addition of acrylonitrile and silylated methacrylate monomers i.e. 2-MAETMS and 2-MAPTMS respectively, to the polyacrylonitrile radical. Low r_1(AN) in DMSO may therefore be attributed to the greater diffusion of bulky silylated comonomers leading to greater cross propagation as suggested by Nametkin *et al*[8] for acrylonitrile-vinyl-trimethylsilane and acrylonitrile-vinyl-dimethylphenylsilane systems in DMF. It has also been shown that acrylonitrile may be associated with DMF[10] being similar in polarity and dielectric constant. So a third kind of acrylonitrile monomer species may be expected in this series of experiments for polymerization. The change in r_1(AN) with changing solvent may reflect the competition between the different species in propagation rates. The drop in r_2(2-MAETMS or 2-MAPTMS) in DMSO also confirms the greater diffusion of these bulky monomers in a more polar medium and enhanced cross-propagation rate. However, higher r_1 and r_2 values

TABLE 3—REACTIVITY RATIO VALUES FOR ACRYLONITRILE-[2-METHACRYLOYLOXY)-ALKOXY] TRIMETHYLSILANE SYSTEMS AT 60°

Monomer pair	Medium	r_1	r_2
AN-2-MAETMS	DMF	0.229±0.02	1.018±0.10
AN-2-MAETMS	DMSO	0.198±0.01	0.468±0.01
AN-2-MAPTMS	DMF	0.485±0.02	1.157±0.03
AN-2-MAPTMS	DMSO	0.216±0.01	0.894±0.01

TABLE 4—REACTIVITY RATIOS AND ARRHENIUS PARAMETERS FOR AN-2-MAETMS SYSTEM IN DMF

Monomer reactivity ratio	Polymerization Temperature, °C 50	60	70	Difference in energies of activation kJ $mole^{-1}$	Ratio of frequency factors	Difference in entropies of activation Jk^{-1} $mole^{-1}$
r_1(AN)	0.361±0.04	0.229±0.02	0.124±0.01	51.46±0.4	0.06±0.01	-23.16±0.3
r_2(2-MAETMS)	0.610±0.09	1.018±0.10	1.882±0.12	-22.53±0.3	1.82±0.01	4.92±0.1

have been observed in DMSO for AN-HEMA and AN-HPMA systems in comparison to the values obtained in DMF[18]. The change in reactivity ratio values after silylation of HEMA and HPMA may be due to the change in polarity of these silylated monomers.

Temperature dependence of reactivity ratios: A study of the temperature dependence of the reactivity ratios for AN-2-MAETMS system in DMF reveals that r_1 decreases and r_2 increases with increase in the copolymerization temperature (Table 4). A similar trend has been observed in styrene-2-MAETMS[6] and styrene-vinylmethyl diacetoxysilane[7] systems. However, r_2(2-MAETMS) increases with increase in the polymerization temperature. At higher temperatures, greater solvation and diffusion of the bulky silylated monomer would enhance both the rate of cross-propagation and self propagation i.e. $K_{12} > K_{11}$ and $K_{22} > K_{21}$, which explains the decrease in r_1 and increase in r_2 values with increase in the polymerization temperature. Arrhenius parameters are given in Table 4. The activation energies $(E_{12} - E_{11})$ favour self propagation of the polyacrylonitrile radical whilst the ratio of pre-exponential factors favours cross-propagation. For the 2-MAETMS radical, the difference $E_{22} - E_{21}$ is 51.46 kJmole^{-1} favouring cross-propagation but A_{22}/A_{21} favours self-addition.

Polymer characterization ·

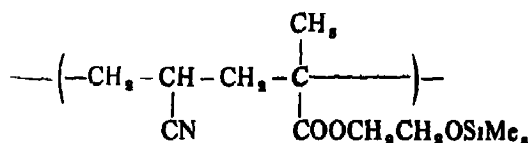
Solubility · The introduction of silylated methacrylates comonomer influences the solubility of polyacrylonitrile in polar and nonpolar solvents. The solubility of PAN in DMF is 12.9 g/100 ml at 30°. By introducing 15.5 mole % of 2-MAETMS and 13.2 mole % 2-MAPTMS in PAN backbone, the solubility of copolymers decreases from 12.9 g/100 ml to 10.7 g and 9.9 g/100 ml respectively at 30° in DMF. In a similar manner, the solubility of PAN and its copolymers viz. AN-2-MAETMS (m_2 = 15.5 mole %) and AN-2-MAPTMS (m_2 = 13.2 mole %) in DMSO are 13.2, 10.4 and 10.1 g/100ml at 30°. However, PAN was found to be insoluble in toluene, whereas AN-2-MAPTMS (m_2 = 13.2 mole %) copolymers show 0.8 g and 0.5 g/100 ml solubilities in toluene at 30°.

Softening range: Polyacrylonitrile shows colour change from yellow to brownish between 220-240° and then turns black above 260°. Poly(AN-2-MAETMS) and poly(AN-2-MAPTMS) copolymers show colour change from yellow to red between 180-200° along with softening and above 240-250°, they attain deep red colour.

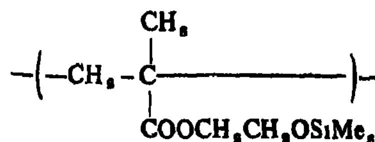
Intrinsic viscosity: The intrinsic viscosity of acrylonitrile copolymers increases with increase in 2-MAETMS or 2-MAPTMS comonomer content (Tables 1 and 2). This may be due to the higher reactivity of the growing silane radical ($\sim\dot{M}_2$) present at the growing chain end which will enhance the rate of propagation, as shown in Fig. 1. Further the change in intrinsic viscosity due to the introduction of silylated comonomers may be related with the change in hydrodynamic volume in such copolymer systems.

Infrared spectra: IR spectra of AN-2-MAETMS and AN-2-MAPTMS copolymers show characteristic absorption bands of acrylonitrile and silylated methacrylate comonomer. A strong band at 1240 and 1250 cm^{-1} in AN-2-MAPTMS and AN-2-MAETMS copolymers respectively confirms the formation of copolymer. Other bands observed are at 763-769 and 840 cm^{-1} due to trimethylsilyl group. A strong band at 1111 cm^{-1} due to Si–O–C has also been observed. The aliphatic C–H bands at 2959 and absorption at 2260 cm^{-1} due to nitrile group have also been observed. However, the absorption bands at 1695 and 1754 cm^{-1} may be due to the presence of cyclic structures. Grassie and associates[20] have also assigned these bands to cyclic structures in their study of heat treated polyacrylonitrile. Quantitative analysis of AN-2-MAETMS copolymers by ir spectra permit us to estimate the copolymer composition. The amount of AN in one of the copolymer was found to be 75 mole % AN against 72.6 mole % AN obtained by elemental analysis. However, for calculating reactivity ratios, compositions based on silicon contents were used.

Proton magnetic resonance spectra PMR spectra of radically initiated PAN is identical with those reported by Murano and Yamadera[21]. In the copolymer there is a multiplet in the region 7.62-8.5 τ due to methylene protons of the polymer backbone and to quinlet due to methine proton in the range of 6.4-7.6 τ. A sharp singlet at 9.8 τ is associated with Me_3Si protons. Presence of a triplet



at 8.8 τ confirms the presence of C–CH_3 protons. Two broad peaks at 6.25 τ and 5.9 τ may be releated to CH_2O protons present in silylated methacrylate. Presence of two signals clearly indicates the nonequivalence of the two CH_2O groups due to different neighbouring groups:

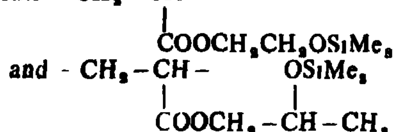


Differential scanning calorimetry (DSC): DSC data for PAN and its copolymers are given in Table 5. Two distinct endothermic transitions have been observed, one occurring at about 71 to 87° and the other at 129 to 131°. Kimmel and Andrews[22] have proposed the concept of a heterobonded solid-state structure to explain these glass transitions. They have suggested that transition at the lower

Table 5—DSC Analysis of PAN Copolymers

Polymer	m_2 in copolymer	Endotherms I	Endotherms II	Exotherm peak maxima	ΔH $cal g^{-1}$
PAN	—	87	131	293	111
P(AN-2-MAETMS)	8.2	88	131	324	127
P(AN-2-MAETMS)	15.5	77	129	333	144
P(AN-2-MAPTMS)	7.8	81	129	328	137
P(AN-2-MAPTMS)	13.2	71	129	337	150

temperature was the result of chain mobility caused by weakening of the Van der Waals forces, while the transition at the higher temperature resulted from intermolecular dipole-dipole dissociation of the nitrile groups in more localized sections of the chain. The T_g values of AN copolymers are lower in comparison to the PAN. A decrease in T_g may be due to the introduction of bulky silicon side substituents



which reduces the intermolecular interactions between the molecular chains. The results of DSC are illustrated in Fig. 5. The sharp exotherm for PAN becomes broader and also shifts to higher temperatures with the introduction of silylated comonomers. It is interesting to note that in P(AN-2-MAPTMS) with higher content of silylated comonomer (13.2 mole %), a small shoulder at 352° along with the main exothermic peak at 337° also appears The quantitative measurements show that the total amount of heat evolved between 270-400°, to be associated with the nitrile group oligomerization, is also dependent on the composition of the polymer. Typical results are reported in Table 5. The occurrance of the broad exotherm in copolymers at higher temperatures than that for polyacrylonitrile indicates the delayed initiation and show propagation of nitrile oligomerization due to the introduction of bulky silylated side substituents. Shifting of the exotherm to higher temperature with increase in the size of side substituents in case of AN-2-MAPTMS copolymers further substantiates the role of steric factors in cyclization.

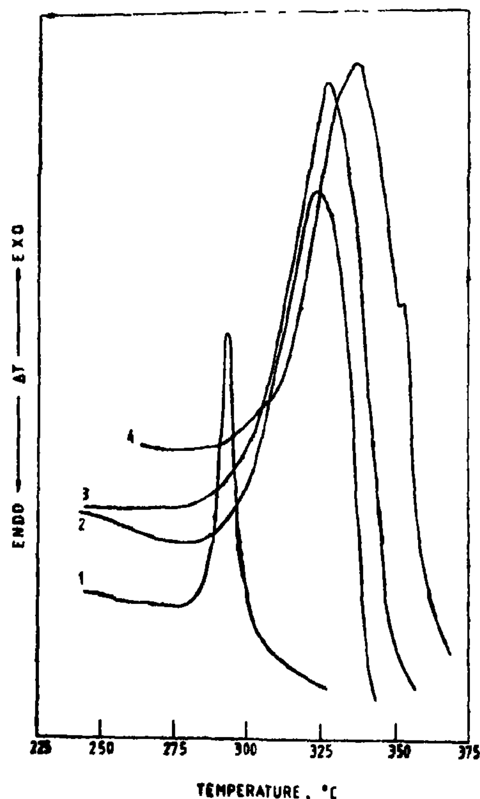


Fig. 5. DSC thermograms of
(1) PAN
(2) AN-2-MAETMS copolymer, (m_2=8.2 mole%)
(3) AN-2-MAPTMS copolymer, (m_2=7.8 mole%)
(4) AN-2-MAPTMS copolymer, (m_2=13.2 mole%)
at heating rate of 20°/min.

Grassie *et al*[22] have already shown that the nitrile oligomerization can be initiated through a molecular mechanism by the carboxylic group of the acid unit. After the first step, an amide structure is formed by isomerization following molecular propagation, while radical propagation is assumed in pure polyacrylonitrile. Similarly, in the present study the presence of silylated side substituents will change the mode of initiation and propagation of nitrile oligomerization thereby leading to broader exotherms at higher temperatures. This also accounts for observed changes in ΔH values.

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Reactions of Coordinated Oximes—Part V : Reactions of Aluminium Isopropoxide on Some Cobalt(II) *Bis*-Chelates of *o*-Hydroxy Oximes

INDRA RANI, K. B. PANDEYA and R. P. SINGH

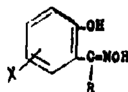
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Cobalt(II) *bis*-chelates of some *o*-hydroxyketoximes have been prepared and characterised by analytical and magnetic susceptibility measurements. They form planar *bis*-chelates with cobalt(II) ions. The further reactions of these cobalt(II) *bis*-chelates with aluminium isopropoxide have been carried out and were studied by analytical and magnetic susceptibility measurements. The tetraisopropoxy derivatives are proposed to have a six-coordinate tetragonal structure.

STUDIES on the metal-chelates of the oxime ligands are important in view of their possible applications as biological models[1,2] and as semiconducting materials[3,4]. Also, the *bis*-chelates of the vic-dioximes and *o*-hydroxyoximes involve short inter-ligand hydrogen bond and packing configurations which give rise to unusual optical properties. The protons involved in the inter-ligand hydrogen bonding are labile and are suitable for the reactions with a variety of reagent. The reactions of boron halides[5] and some organoaluminium compounds[6] with nickel(II) and palladium(II) *bis*-chelates of dimethylglyoxime and salicylaldoxime have been reported.

In continuation to our work[7-10] on reactions of metal alkoxides on coordinated oximes we report in this paper the reactions of aluminium isopropoxide on cobalt(II) *bis*-chelates of some *ortho*-hydroxy oximes viz.,

(i) 2-hydroxy benzaldoxime ($salH_2$), Ia ;
(ii) 2-hydroxy-3-methoxy benzaldoxime ($vanH_2$), Ib ;
(iii) 2-hydroxy-5-methyl acetophenoneoxime ($hmaH_2$), Ic ;
(iv) 2-hydroxy-5-methyl propiophenoneoxime ($hmpH_2$), Id, and
(v) 2-hydroxy-5-methyl butyrophenoneoxime ($hmbH_2$), Ie



(I)

(a) X=H, R=H
(b) $X=3\text{-}OCH_3$, R=H
(c) $X=5\text{-}CH_3$, $R=CH_3$
(d) $X=5\text{-}CH_3$, $R=C_2H_5$
(e) $X=5\text{-}CH_3$, $R=C_3H_7$

In all the cases the bridging protons are replaced by $Al(OPr^i)_2$ groups. Also cobalt achieves six-coordination through axial coordination by the propoxide groups.

Experimental

Aluminium isopropoxide was obtained[11] by the reaction of isopropanol on aluminium foil in presence of catalyst ($HgCl_2$) and was purified by distillation at reduced pressure at ~110°. The ligands were prepared by the literature method[12]. The *bis*-chelates were prepared by mixing aqueous solution of metal salts and alcoholic solution of the respective ligands in molar ratio 2 : 1 and adjusting the *p*H to ~6.0 with sodium acetate. In all cases the complexes separated out and were filtered, washed with water and 50% alcohol and dried in an electric oven.

Reactions of cobalt(II) bis-*chelates with aluminium isopropoxide* : A benzene solution of aluminium isopropoxide was added to the cobalt(II) *bis*-chelates in 2 : 1 molar ratio in each case. On refluxing the contents the following colour changes were observed :

$Co(salH)_2$ - from brown to dark brown,
$Co(vanH)_2$ - from orange to brown,
$Co(hmaH)_2$ - from yellow to dark brown,
$Co(hmpH)_2$ - from yellow to dark brown, and
$Co(hmbH)_2$ - from yellow to dark brown.

Refluxing in all the cases was continued for about 6 hr. The benzene-propanol azeotrope was collected (72°) and analysed for propanol content. The excess solvent was removed first by distillation at atmospheric pressure and then under reduced pressure. The reaction product was finally dried in vacuum over P_4O_{10}.

The alcohol contents were determined by indirect iodometric titration with potassium dichromate and cobalt contents were determined by titration against standard EDTA solution using xylenol orange as indicator.

Magnetic susceptibility measurements on solid complexes were made by Gouy method using tetrathiocyanatocobaltate as calibrant ($\chi_g = 16.44 \times 10^6$ cgs units).

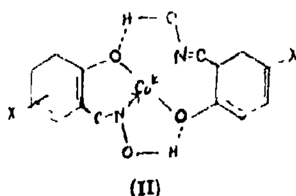
TABLE 1—COLOUR, COMPOSITION AND MAGNETIC PROPERTIES OF TETRAISOPROPOXY DERIVATIVES OF COBALT(II) COMPLEXES

Reactants	Molar ratio	Product, state and colour	Benzene+propanol azeotropy Found (Calcd.)	Elemental analysis Found (Calcd.)			μ_{eff} B.M.	
				%N	%Al	%Co	Benzene	Solid
$Co(salH)_2+Al(OPr^i)_3$ (2.09 g)+(3.62 g)	1 : 2	$Co[sal.Al(OPr^i)_3]_2$, solid, dark brown	0.74 (0.77)	4.43 (4.52)	8.62 (8.78)	9.41 (9.52)	*	3.51
$Co(vanH)_2+Al(OPr^i)_3$ (2.42 g)+(2.52 g)	1 : 2	$Co(van\ Al(OPr^i)_3]_2$, solid, dark brown	0.71 (0.74)	4.02 (4.12)	7.72 (7.95)	8.50 (8.68)	*	3.49
$Co(hmaH)_2+Al(OPr^i)_3$ (2.92 g)+(3.07 g)	1 : 2	$Co[hma.Al(OPr^i)_3]_2$, solid, dark brown	0.86 (0.90)	4.28 (4.15)	8.12 (8.00)	8.61 (8.78)	3 88	3.42
$Co(hmpH)_2+Al(OPr^i)_3$ (2.52 g)+(2.47 g)	1 2	$Co[hmp\ Al(OPr^i)_3]_2$, solid, dark brown	0.70 (0.72)	3 67 (3.98)	7.59 (7.68)	8.19 (8.38)	3.82	3.41
$Co(hmbH)_2+Al(OPr^i)_3$ (2.62 g)+(2.41 g)	1 : 2	$Co[hmb.Al(OPr^i)_3]_2$, solid, dark brown	0.68 (0 70)	3.70 (3.88)	7.29 (7.88)	8.00 (8.06)	3.87	3.53

* The compounds are insoluble.

Results and Discussion

The *bis*-chelates show room temperature magnetic moments of 2.2-2.3 B.M. corresponding to planar cobalt(II). *Bis*-chelates of the *ortho*-hydroxyoximes are known[13] to have planar structure (II) which derives extra stability from additional rings formed through inter-ligand hydrogen bonding.



(II)

The stoichiometry of the reaction with $Al(OPr^i)_3$ is shown in Table 1. Analysis of benzene propanol azeotrope in all the cases correspond to the reaction of two moles of aluminium isopropoxide with one mole of metal chelate yielding two moles of propanol. This stoichiometry is shown in reaction (1) abbreviating all the six ligands as LH_2.



$$Co(LH)_2+2Al(OPr^i)_3 \rightarrow Co[L\text{-}Al(OPr^i)_2]_2+2HOPr^i \quad (1)$$

The two inter-ligand hydrogen bridges of $Co(LH)_2$ are replaced by two $Al(OPr^i)_2$ groups. All the compounds give consistent analysis for $Co[L\text{-}Al(OPr^i)_2]_2$.

The reaction products show magnetic moment of 3.4-3.5 B.M. in solid state and 3.8-3.9 B.M. in benzene solutions (wherever soluble). These values suggest that the square-planar geometry of the parent chelate is not retained. Obtaining of six-coordinate tetragonal structure by involving the terminal isopropoxy groups into coordination seems to be the most plausible interpretation to the observed magnetic moments. For such a geometry, cobalt(II) complexes (ground state $^4T_{1g}$) should show[14] magnetic moments corresponding to three unpaired spins. The experimental values are known to lie upto 5.0 due to spin orbit coupling. Subnormal magnetic moments in the present compounds are obtained due to spin-coupling between two cobalt atoms through the O–Al–O bridges (Fig. 1).

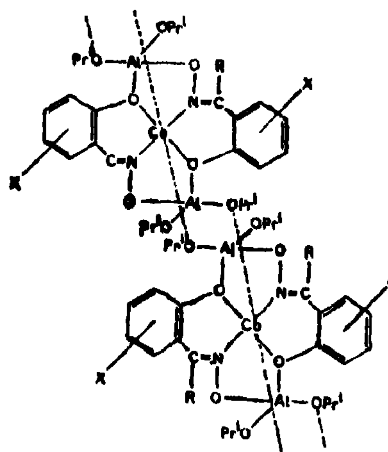


Fig 1

The complexes react with water to convert into tetrahydroxo species with release of isopropanol as shown below ·



$$Co[L-Al(OPr^i)_2]_2+4H_2O \rightarrow Co[L-Al(OH)_2]_2+4HOPr^i$$

But the tetrahydroxo species are very much stable and do not break into the parent chelates even on boiling with water. This extra stability of tetraisopropoxy derivatives to the corresponding nickel(II) derivatives may be attributed to the stable cage formed through the O–Co–O–Al–O–Co–O bridges.

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Halogen Oxidation and Nitrosylation of Mixed Ligand Molybdenum and Tungsten Tricarbonyls

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$(L\text{-}L)(Ph_3E)Mo(CO)_3$ (L-L = *o*-phen or 2,2'-bipy ; E = As or Sb) after bromine or iodine oxidation yield $[(L\text{-}L)(Ph_3E)Mo(CO)_3X]X$ (X = Br, I) derivatives. Under similar conditions Ph_3P is displaced from $(L\text{-}L)(Ph_3P)Mo(CO)_3$ to produce dimeric $(L\text{-}L)Mo(CO)_3X_2$. Chlorine swept benzene displaces both CO and Ph_3P from $(L\text{-}L)(Ph_3P)Mo(CO)_3$ and only CO from $(L\text{-}L)(Ph_3E)Mo(CO)_3$ to yield $(L\text{-}L)MoCl_4$ and $[(L\text{-}L)(Ph_3E)MoCl_3]Cl$, respectively. Nitrosylation of $(L\text{-}L)(Ph_3E')M(CO)_3$ (M = Mo, W ; E' = P, As, Sb) using NOCl gives a mixture of $(L\text{-}L)M(NO)_2Cl_2$ and $[(L\text{-}L)M(CO)_2(NO)_2Cl]Cl$; while $[(L\text{-}L)M(CO)_2(NO)]_2$ derivatives are recovered when free NO is used.

The complexes have been characterised by elemental analysis, ir, conductivity and magnetic measurements.

SEVERAL studies have been made on the halogen oxidation of penta- and tetra-carbonyls of group VI metals but relatively little attention[1,2] has been paid to tricarbonyls, particularly to those containing two different non-carbonyl ligands. A few recent investigations on some $(L-L)LM(CO)_3$ (L−L = *o*-phen or 2,2'-bipy ; L = amine molecule ; M = Mo, W) derivatives exhibited very striking results due to the formation of complexes of unusual stoichiometry[3,4]. These products are thought to be either seven-coordinate complexes with bidentate ligands (L−L) acting as monodentate or seven-coordinate 1 : 1 adducts with $(L-L)LM(CO)_3$ species acting as Lewis bases and molecular halogens as Lewis acids. To examine the nature of products formed as a result of chlorination, bromination and iodination of analogous Ph_3P, Ph_3As and Ph_3Sb derivatives, the complexes $(L-L)(Ph_3E')Mo(CO)_3$ (E' = P, As or Sb) have been used in the present investigation.

To explore the possibility of formation of nitrosyl carbonyl derivatives of group VI metals, nitrosylation of these mixed ligand derivatives and analogous tungsten complexes has also been attempted using both nitrosonium cation (NO^+) and free NO.

Experimental

General : All the experiments were performed in dry nitrogen. $(L\text{-}L)M(CO)_3$ derivatives were prepared by the methods given in literature[8,9]. Nitrosyl chloride was prepared by the method described in literature[10] and nitric oxide was prepared by the action of sodium nitrite on acidified ferrous sulphate solution and was purified by passing through 50% NaOH solution. Halogens were estimated gravimetrically by precipitating the corresponding silver salt. Conductivity measurements were made on a Toshniwal conductivity bridge (model 302) using nitrobenzene or acetone as solvent. Magnetic measurements were done with polytronic Electromagnetic Type EM-100, SR No 113 using Keroy magnetic balance with sensitivity 10^{-5}g. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 337 in KBr discs.

Reaction of o-phenanthroline(triphenylphosphine)-tricarbonylmolybdenum(O) with iodine A benzene solution of iodine (0.13 g) was added dropwise to a solution *o*-phenanthroline(triphenylphosphine)-tricarbonylmolybdenum(O) (0.30 g) in benzene (75 ml) under nitrogen at ambient temperature with constant stirring of the reaction mixture. A grey precipitate slowly appeared and the reaction mixture was set aside for further 4 hr to ensure complete precipitation. Liberation of CO did not take place during the reaction. The precipitate was filtered and washed well with several 10 ml portions of benzene to remove traces of iodine or parent carbonyl, if left unreacted. The product was dried *in vacuo*. Yield 55.5%. Anal. Found : C, 30.2; H, 2.0 ; N 4.8 ; I, 40.1. $C_{30}H_{16}Mo_2N_4O_6I_4$ requires C, 29.3 ; H, 1.3 ; N, 4.6 ; I, 41.3%.

Colour, yield, ν_{C-O}, mol. conductivity and analytical data of different halocomplexes prepared under similar conditions (but by using different halogens and appropriate carbonyls) are given in Table 1.

Reaction of o-phenanthroline(triphenylphosphine)-tricarbonylmolybdenum(O) with NOCl : A dilute benzene solution of NOCl was added drop by drop on solid *o*-phenanthroline(triphenylphosphine)-tricarbonylmolydenum(O) (0.2 g) under nitrogen at room temperature with constant stirring of the reaction mixture.* Slow dissolution of the solid mass took place followed by the precipitation of a yellow red solid. After 1 hr of stirring the colour of the supernatant liquid became paddy green and the solid (product A) settled down at the bottom of the reaction vessel. The supernatant liquid was

TABLE 1—CHARACTERISTIC, PHYSICAL AND ANALYTICAL DATA OF HALOCOMPLEXES

Complexes	Colour	Yield %	νCO(cm⁻¹) (KBr disc)	Λm ohm⁻¹ cm² (acetone)	Analysis(%) Found(Calcd.) C	H	N	X
[(o-phen)Mo(CO)$_3$Br$_2$]$_2$	brown	48.4	2040wsh, 2080s, 1975s, 1950s, 1940s, 1910w, 1898s		35.8 (34.6)	1.9 (1.5)	5.2 (5.4)	28.2 (30.7)
[(2,2′-bipy)Mo(CO)$_3$I$_2$]$_2$	grey	56.8	2040wsh, 2028s, 1972s, 1950s, 1920vw, 1915m, 1892s		26.9 (26.1)	1.8 (1.8)	4.8 (4.7)	42.5 (43.0)
[(2,2′-bipy)Mo(CO)$_3$Br$_2$]$_2$	brown	49.3	2045wsh, 2028s, 1980s, 1942s, 1920vw, 1910w, 1905s		30.3 (31.5)	1.4 (1.6)	5.2 (5.6)	30.8 (32.2)
[(o-phen)(Ph$_3$As)Mo(CO)$_3$I]I	grey	57.3	2030s, 1958s, 1905s	60.4	42 2 (43 0)	2.1 (2.5)	2.9 (3.0)	26.1 (27.5)
[(o-phen)(Ph$_3$As)Mo(CO)$_3$Br]Br	yellow orange	48.3	2055s, 1978s, 1915s	63.8	46.1 (47.9)	2.2 (2.7)	3.5 (3.3)	18.8 (19.4)
[(o-phen)(Ph$_3$Sb)Mo(CO)$_3$I]I	grey	56.2	2040s, 1978m, 1898vs	61.2	39 8 (40.8)	2.1 (2.4)	2.5 (2.9)	25.2 (26.3)
[(o-phen)(Ph$_3$Sb)Mo(CO)$_3$Br]Br	brown	49.2	2055s, 1975s, 1910vs	65.3	43.2 (45.3)	2.4 (2.6)	2.9 (3.2)	17.5 (18.3)
[(2,2′-bipy)(Ph$_3$As)Mo(CO)$_3$I]I	grey	56 6	2020ms, 1955s, 1905s	59.6	38.6 (41.5)	2.2 (2.5)	2.5 (3.1)	27.2 (28.3)
[(2,2′-bipy)(Ph$_3$As)Mo(CO)$_3$Br]Br	orange	46.3	2055vs, 1980s, 1915s	64 8	44.8 (46 3)	1.9 (2.8)	3.1 (3.4)	16.3 (17.1)
[(2,2′-bipy)(Ph$_3$Sb)Mo(CO)$_3$I]I	grey	57.5	2020s, 1952ms, 1900ms	56.8	37 3 (39.3)	2.1 (2.4)	3.4 (2.9)	24.1 (26.9)
[(2,2′-bipy)(Ph$_3$Sb)Mo(CO)$_3$Br]Br	orange	45.3	2050s, 1975s, 1922s	65 6	41.6 (43.8)	2.2 (2.7)	2.8 (3.3)	17.5 (18.8)
(o-phen)MoCl$_4$	yellow	74 2			32 6 (34.4)	1.5 (1.9)	6.2 (6.6)	30.2 (33.9)
[(o-phen)(Ph$_3$As)MoCl$_3$]Cl	yellow	75.3		60.4	48.1 (47.7)	2 5 (3.2)	3.1 (3.8)	18.2 (19.6)
[(2,2′-bipy)(Ph$_3$As)MoCl$_3$]Cl	yellow	73.8		62.2	52 1 (53.2)	3.2 (3.3)	4.8 (4.1)	19.8 (20.3)
[(o-phen)(Ph$_3$Sb)MoCl$_3$]Cl	yellow	72.3		60.2	45.5 (46.7)	2 1 (2.0)	3.5 (3.6)	17.6 (18.1)
[(2,2′-bipy)(Ph$_3$Sb)MoCl$_3$]Cl	yellow	74.3		62.3	46.3 (49.8)	2 3 (3.1)	3.2 (3.7)	18.9 (19.0)

TABLE 2—CHARACTERISTIC, PHYSICAL AND ANALYTICAL DATA OF VARIOUS COMPLEXES

Complex	Colour	Yield %	νCO(cm⁻¹) (KBr disc)	νNO (cm⁻¹)	Λm ohm⁻¹ cm² (in acetone)	Analysis (%) Found(Calcd.) C	H	N	Cl
[(Ph$_3$As)Mo(CO)$_2$(NO)$_2$Cl]Cl	Yellow-red	40.2	2040s, 1930s	1785s, 1660s	65.5	38.7 (40.8)	2.1 (2.5)	4.5 (4.8)	11.5 (12.0)
[(Ph$_3$Sb)Mo(CO)$_2$(NO)$_2$Cl]Cl	Yellow-red	41.7	2035s, 1925s	1780s, 1660s	68.7	35.3 (37.3)	2.0 (2.3)	4.0 (4.4)	10.7 (11.0)
[(Ph$_3$P)W(CO)$_2$(NO)$_2$Cl]Cl	Yellow	38.5	2030s, 1925s	1780s, 1660s	82.2	35.3 (38.0)	2.0 (2.4)	4.0 (4.4)	10.7 (11.2)
[(Ph$_3$As)W(CO)$_2$(NO)$_2$Cl]Cl	Yellow	38.2	2030s, 1920s	1780s, 1665s	78 0	33.1 (35.5)	1.8 (2.2)	3.2 (3.1)	9.1 (10.5)
[(Ph$_3$Sb)W(CO)$_2$(NO)$_2$Cl]Cl	Yellow	40 0	2030s, 1920s	1772s, 1652s	80.5	31.0 (33.1)	1.8 (1.7)	2.9 (2.9)	9.0 (9.8)
[(2,2′-bipy)Mo(NO)$_2$Cl$_2^{*}$]	Green	30.8-42.4		1775s, 1660s, 1625sh	5.8	28.3 (30.7)	2.8 (2.1)	13.1 (14.6)	17.5 (18.5)
[(o-phen)W(NO)$_2$Cl$_2^{**}$]	Green	27.0-34.3		1745s, 1645s, 1635sh	7.0	27.3 (29.1)	2.0 (1.6)	10.1 (11.3)	12.8 (14.8)
[(2,2′-bipy)W(NO)$_2$Cl$_2^{**}$]	Green	30.4-36.0		1745s, 1650s, 1640s	6.2	24.0 (25.5)	2.0 (1.7)	11.0 (11.9)	14.8 (15.1)

* reported ν_{N-O} 1790s, 1695s (Ref. 11).
** IR bands in nujol mull (others in KBr).

decanted out under nitrogen. A paddy green solid (product B) was precipitated from this solution by adding hexane (60 ml). Product B was washed several times with hexane and was dried *in vacuo*. It was shown to be dichloro (*o*-phenanthroline) dinitrosylmolybdenum(II). Anal. Found : C, 32.3 ; H, 2.2 ; N, 12.9 ; Cl, 17.0. $C_{12}H_8N_4O_2MoCl_2$ requires C, 35.4 ; H, 2.0 ; N, 13.0 ; Cl, 17.4%. ν_{N-O} : 1785s, 1688s, 1655sh cm⁻¹, reported bands[11] 1790s, 1685s cm⁻¹.

Product A was washed several times with benzene to remove parent *o*-phenanthroline (triphenylphosphine)tricarbonylmolybdenum(O) (practically nil) and dichloro(*o*-phenanthroline)dinitrosylmolybdenum(II) and was dried *in vacuo*. It was shown to be chloro(triphenylphosphine)dinitrosyldicarbonylmolybdenum(II) chloride: (yield 0.074 g, 42.2%). Anal. Found: C, 41.2; H, 2.4; N, 5.3; P, 5.2; Cl, 12.5. $C_{20}H_{15}O_4N_2PMoCl_2$ requires C, 44.0; H, 2.8; N, 5.1; P, 5.7; Cl, 13.0%; m.p. 163-55°d in sealed capillary, ν_{C-O} 2035s, 1920s cm^{-1}, ν_{N-O}: 1778s, 1640s cm^{-1}, $\Lambda_M=70.2$ ohm^{-1} cm^2(in acetone). It dissolved only in polar solvents like acetone, methanol, dichloromethane and chloroform and was fairly stable.

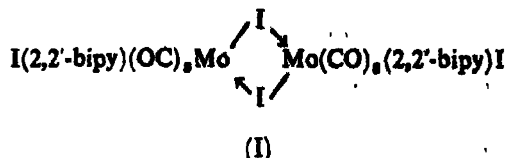
Colour, yield, ν_{C-O}, ν_{N-O}, molecular conductivity and analytical data of other derivatives are given in Table 2.

Reaction of o-phenanthroline(triphenylphosphine)-tricarbonylmolybdenum(O) with nitric oxide: Nitric oxide, free from nitrogen peroxide, was absorbed in benzene and the solution was added dropwise on solid *o*-phenanthroline(triphenylphosphine)tricarbonyl(O) (0.2 g) at room temperature under an atmosphere of nitrogen with constant stirring of the reaction mixture. The violet colour of the solid mass disappeared slowly with the dissolution of the parent carbonyl and precipitation of an yellow solid took place. The reaction mixture was set aside for 2 hr and then the precipitate was filtered, washed and dried *in vacuo*. It could not be recrystallised due to its unstable nature in solution. It was shown to be *bis*(*o*-phenanthroline)dinitrosyltetracarbonyldimolybdenum(I), $[(C_{12}H_8N_2)Mo(CO)_2(NO)]_2$, prepared by an alternative method[7]. Anal. Found: C, 44.1; H, 2.4; N, 11.0. $C_{28}H_{16}N_6O_6Mo_2$ requires C, 46.4; H, 2.2; N, 11.6%.

Under similar conditions analogous triphenylarsine and triphenylstibine derivatives yielded the identical compounds.

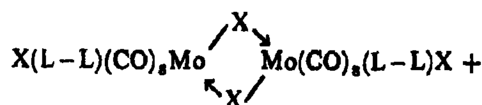
Results and Discussion

Halogen oxidation: Compared to triphenylarsine and triphenylstibine containing complexes, triphenylphosphine derivatives, $(L-L)(Ph_3P)Mo(CO)_3$ behaved differently when subjected to halogen oxidation. They yielded products of stoichiometry $(L-L)Mo(CO)_3X_2$ (X=Br or I) when treated with a benzene solution of bromine or iodine at ambient temperature in nitrogen atmosphere with constant stirring of the reaction mixture. Evolution of CO did not take place in any case. The ir spectra of the resulting complexes exhibited seven bands in the C–O region but the bands of coordinated triphenylphosphine molecule were not present. The appearance of seven CO bands cannot be attributed to any geometry of mononuclear formulation and the possibility of formation of simple $(L-L)Mo(CO)_3X_2$ derivatives is ruled out. Except two extra very weak bands, which might arise due to enhanced molecular interactions in solid state (KBr discs), the spectra are almost identical to that reported by Stiddard[8] for the iodo-bridged dinuclear complex:



(I)

prepared by the action of iodine on (2,2'-bipy)$Mo(CO)_4$ in chloroform at 0° (ν_{CO}: 2040, 2018, 1976, 1935 and 1888 cm^{-1} in $CHCl_3$). Moreover they resembled the complex (I) in the conductivity behaviour. Although, assuming dimeric structures the complexes are expected to exhibit non-ionic behaviour, they gave conducting solutions in nitrobenzene (20.3–21.74 ohm^{-1} cm^2). These values are in comparatively lower range than expected for uni-univalent metal halocarbonyls. Such electrolytic behaviour may be accounted for the well established solvent attack[5] according to the following equilibrium:





Under similar conditions $(L-L)(Ph_3E)Mo(CO)_3$ (E=As or Sb) gave $[(L-L)(Ph_3E)Mo(CO)_3X]X$ (X=Br or I) after bromine or iodine oxidation. The ir spectra of the products exhibited three strong bands in the CO region (Table 1) alongwith the bands of coordinated Ph_3As or Ph_3Sb. The appearance of these ligand bands clearly indicate that, in contrast to the Ph_3P analogues, Ph_3As and Ph_3Sb molecules remain intact through the metal atom even after halogen attack. The molecular conductivity data (Table 1) together with diamagnetic character of these derivatives are in full accordance with their hepta-coordinate cationic structures having molybdenum in the II oxidation state.

Chlorine swept benzene displaced both Ph_3P and CO from $(L-L)(Ph_3P)Mo(CO)_3$ to yield $(L-L)MoCl_4$. The absence of Ph_3P bands from the spectra, their non-electrolytic behaviour and an μ_{eff} of 2.64 B.M. (for both *o*-phen and 2,2'-bipy substituted derivatives) established the neutral and hexacoordinate formulation for the resulting complexes.

It is noteworthy that, similar to bromination and iodination, Ph_3E (E=As, Sb) ligands remained intact through the metal atom in case of chlorination also and products having composition $(L-L)(Ph_3E)MoCl_4$ were isolated in all cases. Such complexes are of rare occurrence; they had not been synthesised hitherto by the action of halogens on metal carbonyl species. The synthesis of a few resembling complexes[6], $ML_2L'X_4$ (M=Mo, W; L=$PPhMe_2$, $PPhEt_2$ and L'=$PPhMe_2$,

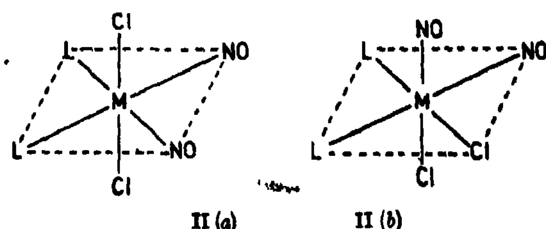
PPh_2Me), has been achieved via another route, i.e., by the action of L′ on ML_2X_4 derivatives under forcing conditions (protracted reflux).

Although these complexes are fairly stable under nitrogen, their slow conversion into unidentified red substances has been noted on exposure to air. In nitrogen swept acetone they exhibited molecular conductivity attributable to uni-univalent electrolytic behaviour (Table 1).

Nitrosylation : Nitrosylation of the mixed ligand tricarbonyls of both molybdenum and tungsten has been studied using both NOCl and free NO.

(L−L) (Ph_3E')$M(CO)_3$ (M=Mo, W ; E′=P, As, Sb ; L−L=*o*-phen, 2,2′-bipy) reacted with a benzene solution of nitrosyl chloride at room temperature under nitrogen to give a mixture of two products [Ph_3E')$M(CO)_2(NO)_2Cl$] Cl and already known (L−L)$M(NO)_2Cl_2$ (details of separation are given in the experimental section). [(Ph_3E')-$M(CO)_2(NO)_2Cl$] Cl derivatives are yellow-red crystalline solids, soluble in polar solvents like dichloromethane, acetone and methanol but do not dissolve in hydrocarbon solvents and light petroleum (40-60°). The nature and number of CO and NO bands in their ir spectra (Table 2), their uni-univalent electrolytic behaviour (Λ_m=65.5-80.5 ohm^{-1}cm^2) and diamagnetic character suggested them to be the hexacoordinate cationic complexes of metal (II).

(L−L)$M(NO)_2Cl_2$ were isolated in the form of an unseparable mixture of two isomers (II *a* and *b*) :



II (*a*) II (*b*)

The ir spectra of (L−L)$M(NO)_2Cl_2$ exhibited two strong and one shoulder bands in the N−O stretching region. On the basis of usual π-bonding effect isomer (*a*) is expected to show higher ν_{N-O} than the isomer (*b*). Intensities of these bands further suggest that isomer (*a*) predominates in case of molybdenum while isomer (*b*) for tungsten complexes.

Nitrosylation of analogous mixed amine-molybdenum tricarbonyls, (L-L) (amine) $Mo(CO)_3$ (amine=$C_4H_9NH_2$, $C_6H_{11}NH_2$, $C_5H_{11}N$ and C_4H_8NO) (solid carbonyl), with a benzene solution of NOCl gave only isomeric mixture of (L-L)-$Mo(NO)_2Cl_2$ and compounds of the type [(amine)-$Mo(CO)_2(NO)_2Cl$] Cl could not be isolated.

On attempting nitrosylation of (L-L)(Ph_3E')-$M(CO)_3$ with a benzene solution of nitric oxide yellow crystalline dinuclear products [(L-L)$M(CO)_2$-$(NO)]_2$ were isolated. Synthesis of identical compounds has already been reported[7] by the action of nitric oxide on (L-L)$M(CO)_4$ or carbonyl-bridged molybdenum derivative [(2,2′-bipy)-$Mo(CO)]_2$.

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Studies on the Coordination Polymer of Niobium(V) with 1,6-Dihyroxyphenazine

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Complexation reaction between niobium(V) and 1,6-dihydroxyphenazine has been investigated with a view to isolate the brown complex and to study its stoichiometry on the basis of elemental analysis, ir spectra, magnetic studies and thermogravimetric analysis. Infrared spectra show 1,6-dihydroxyphenazine acting as a tetradentate ligand coordinating through oxygen and nitrogen since two oxine functions are present in the structure of the ligand. A possible polymeric structure of the complex involving ligand and anion bridge has been suggested.

NEED for new polymeric material with good thermal and chemical stability has led to research on many coordination polymers since it is known that reaction of metal ions with organic ligands produces coordinated systems having enhanced thermal stability and often improved chemical resistance.

Studies on the coordination polymers of several metals with tetradentate 1,6-dihydroxyphenazine (DHP) have been reported in literature[1]. Since several Nb(V) compounds have also been found to have polymeric structure, it was considered worthwhile to investigate reaction of DHP with niobium(V) also. Since two oxine functions are present in the ligand, complexation with DHP was expected to lead to interesting coordination products.

Experimental

Pure niobium pentachloride (Fluka) and A. R. grade chemicals were used

Preparation of niobium solution : Niobium pentachloride (1.0 mole) was dissolved in a mixture of dimethylformamide and alcohol (1 : 1). Care was taken to avoid moisture while weighing.

Preparation of the reagent The reagent was obtained from 1,6-dimethoxyphenazine[2] by refluxing the product with hydrobromic and glacial acetic acids for 24 hr[3]. Golden-yellow needles were obtained after two crystallizations from ethylacetoacetate. The compound does not show any sharp melting point and decomposed at 274-275°. Found · C, 67.42 ; H, 3.75 ; N, 13.01. $C_{12}H_8O_2N$ requires C, 67.90 ; H, 3.78 ; N, 13.70%.

Preparation of the coordination polymer : An equimolar mixture of 1,6-dihydroxyphenazine and niobium pentachloride was refluxed in an alcohol-dimethylformamide (1 : 1) mixture for about 2-3 hr. The brown precipitate obtained was filtered and washed with alcohol-DMF mixture and dried at room temperature. The complex does not show a sharp melting point. It is not soluble in common organic solvents like acetone, benzene, chloroform, nitrobenzene, pyridine etc.

Elemental analysis : The chief constituents of the complex were determined by standard methods. The molecular weight of the complex could not be determined because of its insolubility in common organic solvents. Found · C, 21.51 ; H, 0.98 ; N, 3.92 ; Cl, 40.98 ; M, 27.02. $(C_{12}H_6N_2O_2Nb_2Cl_8)_n$ requires C, 21.18 ; H, 0.88 ; N, 4.11 ; Cl, 41.77 ; M, 27.33%.

IR spectra : The ir spectra of 1,6-dihydroxyphenazine show characteristic frequencies pertaining to –OH, –C=N and aromatic characters. The phenolic –OH stretching absorption bands are found in the region 1110 cm^{-1}, 1260 cm^{-1} and 1350 cm^{-1} ; –C=N– absorption peak is found in the region 1650 cm^{-1}, 1560 cm^{-1} and 1280 cm^{-1}. The spectra of the complex is discussed later.

Magnetic studies · Magnetic susceptibility of the complex was measured by Gouy method using mercury(II) tetrathiocyanate cobaltate(II) as the calibrating agent ($\chi g = 16.44 \times 10^{-8}$ cgs units) at 300°K. Pascal's constants were used to correct the measured susceptibility for the diamagnetism of the cation and the ligand[4]. The magnetic moment of the complex was found to be 0 41 B.M. (300°K).

Thermogravimetric analysis. Setaram G–70 Thermoanalyzer (France) was used to study the thermal stability of the coordination polymer. The sample in the 50 mg range was carefully weighed in a platinum crucible and positioned in the centre of furnace. Heating was carried out in oxygen atmosphere. During the entire run the temperature in the immediate vicinity of the sample and weight loss were recorded on previously calibrated chart paper. The per cent weight loss was plotted as a function of temperature. The TG analysis indicates that the complex is stable till 230°. The initial degradation takes place between 230-530°, possibly due to the partial decomposition of the polymer and formation of some oxide. Finally at 530° the polymer is completely converted into niobium pentoxide.

Results and Discussion

Coordination of niobium(V) with 1,6-dihydroxyphenazine is presumed to form a coordination polymer having a possible structure represented in Fig. 1.

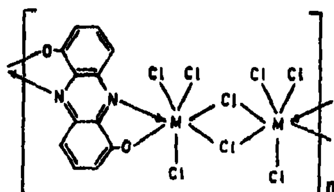


Fig 1.

The ir spectra of the polymer is in close conformity with the above structure.

Significant changes were observed in the spectra of the ligand after complex formation. Phenolic-OH stretching and bending vibrations are absent. The M–O bond is assigned at 925 cm^{-1} in the same way as attributed to the chelate of 8-hydroxyquinoline[5]. The frequency of –C=N vibration in the complex spectra is shifted to lower regions. These suggest involvement of hydroxyl group and N atom in the coordination with the niobium atom.

The terminal Nb–Cl stretching band appears at 342 cm^{-1}. Similar frequency at 340-270 cm^{-1} has been reported for such bond in some other niobium octahedral complexes[6]. Many bands appear in the spectra of the complex at 240 cm^{-1}, 220 cm^{-1} suggesting M–Cl bridging since, in general, bridging M–Cl stretching frequencies are lower than terminal M–Cl stretching frequency[7]. Increase in the coordination number as well as polymeric structure is also considered responsible for the lowering of the bridging frequencies[8].

The insolubility of the complex in common solvents and lowering of bridging M–Cl frequencies lend support to the polymeric nature of the complex as is, in fact, found in the case of polymeric structure of $NbOCl_3^9$.

Interpretation of magnetic susceptibility of the compound of second and third row transition series is more complex since the 4d and 5d orbitals are larger than the 3d orbitals so that the inter-electronic repulsions which tend to oppose spin pairing are less. Also, since the nuclear charges are higher and therefore exert stronger attraction on the ligands, a given set of ligands produces a greater splitting of the d orbitals. The Nb–DHP complex is diamagnetic and the effective magnetic moment (μ_{eff}) has been found to be 0.41 B.M. (300°K). This is far below the purely spin value for an unpaired electron (1.73 B. M.), since the spin orbital effects should be negligible. Thus the little μ_{eff} may be due to only spin-spin interaction between niobium atoms through the chlorine bridge. A number of complexes are reported which are apparently dimeric or polymeric and show only a small paramagnetism[10].

The results of elemental analysis considered along with the ir spectra and magnetic studies indicate the complex to be a linear coordination polymer. Though the thermal stability of this polymer is not high yet its insolubility in common solvents is noteworthy.

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Metal Complexes of Sulphur-Nitrogen Chelating Agents : Transition Metal Complexes of the Esters of 2-Amino-1-cyclopentene-1-dithiocarboxylic Acid

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The complexes of Ni(II), Cu(II), Co(II), Cd(II) and Fe(III) with diethylaminomethyl ester of 2-amino-1-cyclopentene-1-dithiocarboxylic acid, $RHN\overline{CCH_2CH_2CH_2C}$-C(S)SR' [LH when R=H and $R'=CH_2N(C_2H_5)_2$] and Ni(II) with methyl ester of N-methyl acid [L'H when $R=R'=CH_3$] have been synthesized and characterized.

CHELATING species containing both soft and hard potential donor centres when complexed to metal ions are of significance due to diverging reasons. In transition metals the electronic structure and stereochemistry of sulphur-nitrogen ligand complexes are comparatively much less understood[1]. The added interest in them with reference to main group elements and probably also with early transition metals is due to their preferential bond formation with soft or hard donors resulting into what is now known as anisobidentate[2] character of the ligands. With the above view in mind stereochemistry of some later transition metal complexes of the esters of 2-amino-1-cyclopentene-1-dithiocarboxylic acid, $RHN\underline{CCH_2CH_2CH_2C}C(S)SR'$, has been described in the present paper.

Experimental

All the solvents were purified (dried and distilled) by the standard methods. The esters were prepared by the literature methods[3,4]. The infrared spectra were recorded on nujol mull on a Perkin-Elmer-621 spectrophotometer (4000-200 cm^{-1}). The pmr spectra were run on A-60 Varian spectrometer in CCl_4 solution using TMS as an internal standard. The magnetic moment measurements were made at room temperature (308° K) by Gouy's balance and electronic spectra were run in $CHCl_3$ solution on Carry-14 spectrometer. Metal and sulphur analyses were carried out gravimetrically and nitrogen by the Kjeldahl method. The carbon and hydrogen analyses were carried out in our Microanalytical Laboratory. Molecular weights were determined cryoscopically in benzene and nitrobenzene.

General method of the preparation of transition metal complexes of diethylaminomethyl ester of the acid and methyl ester of 2-N-methylamino-1-cyclopentene-1-dithiocarboxylic acid; Methanolic or ethanolic solutions of metal chlorides or acetates [of Ni(II), Cu(II), Co(II), Cd(II) and Fe(III)] were mixed with the solutions of the ligands in tetrahydrofuran (in case of the diethylaminomethyl ester) and in methanol or ethanol (in case of the methyl ester) in appropriate molar ratios. In the case of chlorides the reactions were facilitated by adding a suitable amount of $NaHCO_3$. The metal complexes precipitated were filtered out and washed thoroughly with water. All the compounds (Table 1) were recrystallized from hot tetrahydrofuran or methanol and dried under vacuum at 32-35°/0.1 mm/1 hr.

Results and Discussion

The transition metal complexes of the type, $M[RHN\underline{CCH_2CH_2CH_2C}C(S)SR']_n$, [$R=R'=CH_3$, M=Ni(II) and n=2; R=H, $R'=CH_2N(C_2H_5)_2$, M=Ni(II), Co(II), Cd(II), Cu(II), n=2 and M=Fe(III), n=3] have been synthesized from the corresponding acetates or chlorides. All the complexes are dark coloured crystalline solids with sharp melting points, except of Co(II) and Fe(III) which decomposed, and are soluble only in tetrahydrofuran and nitrobenzene. The complexes of Ni(II) with the methyl ester of 2-N-methylamino-1-cyclopentene-1-dithiocarboxylic acid is soluble in all common organic solvents. All of these are found to be monomeric (cryoscopically).

In the ir spectrum of diethylaminomethyl ester the presence of a broad band of $\nu(N-H)$ at 3290 cm^{-1} and absence of $\nu(N-H)$ band in the spectrum of methyl ester show the existence of the following structures (Ia or Ib) which is also supported by the absence of $\nu(S-H)$ band in the 2550-2650 cm^{-1} region in them[4]. The spectra of both the esters[4] show strong to medium intensity bands of $\nu(C=S)$ at 1270±5, 1155±5 cm^{-1} along with $\nu(C=N)$ and at 725 cm^{-1}.

TABLE 1—TRANSITION METAL COMPLEXES OF THE ESTERS OF 2-AMINO-1-CYCLOPENTENE-1-DITHIOCARBOXYLIC ACID

Sl. No.	Products* colour	m.p. (°C)	Analysis(%) Found(Calcd.) C	H	M	S	N	μ_{eff} 303° (B.M.)	Molecular weight Found (Calcd.)
1.	L_2Ni Bright brown	155-57	48.99 (48.61)	7.82 (7.02)	10.26 (10.76)	23.10 (23.51)	10.10 (10.27)	Diamagnetic	568 (545.4)
2.	L_2Cu Dark blue	270-72	48.61 (48.00)	7.48 (7.30)	11.84 (11.54)	23.61 (23.26)	10.08 (10.18)	1.90	574 (550.3)
3.	L_2Co Black	above 360[d]	—	—	—	23.11 (23.49)	10.42 (10.27)	2.12	571 (545.7)
4.	L_2Cd Olive	320-21	—	—	18 67 (18.33)	21.01 (21.40)	9.18 (9.35)	Diamagnetic	574 (599.2)
5.	L_3Fe Light brown	above 360[d]	50.80 (50.42)	7.53 (7.31)	7.35 (7.11)	25.25 (24.47)	10.98 (10.69)	5.35	808 (785.9)
6.	L'_2Ni**	183-84	—	—	13.04 (13.63)	30.16 (29.84)	6.67 (6.50)	Diamagnetic	455.6 (430.7)

$L=HN\overline{CCH_2CH_2CH_2C}C(S)SCH_2N(C_2H_5)_2$ and $L'=CH_3N\overline{CCH_2CH_2CH_2C}C(S)SCH_3$

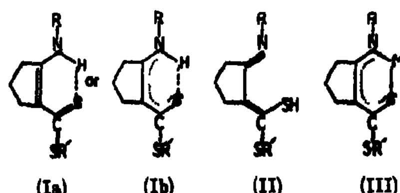
* Crystalline solids, yields, 85-90%. Molecular weights were determined for the compounds Sl. No. 1-5 in nitrobenzene and for Sl. No. 6 in benzene cryoscopically.

** PMR values (in ppm) for SCH_3 (2.63), 3,5-CH_2 (2.90), 4-CH_2 (1.95) and NCH_3 (3.15).

TABLE 2—ELECTRONIC SPECTRAL DATA (in cm^{-1}) OF THE TRANSITION METAL COMPLEXES

LH	L'H	L_2Ni	L_2Cu	L_2Co	L_2Cd	L_3Fe	L'_2Ni	Assignments
25,510	25,252							$\pi-\pi^*$
30,769	31,545							
38,168								
				11,430				d-d
						11,525		d-d($^6A_{1g}\rightarrow{}^4T_{1g}$)
		16,000	16,667	16,000			16,100	d-d($^1A_{1g}\rightarrow{}^1A_{2g}$) ($MN_2S_2$ chromophore)
		20,000					21,740	d-d($^1A_{1g}\rightarrow{}^1B_{1g}$)
		24,570	30,731	24,510	24,000	24,540	25,126	L−L* (L−M or M−L)
		30,120	32,051	30,030	32,260	30,050	31,444	
		37,037	44,440	37,037	37,037	37,042		
		45,540						

$L=HN\overline{CCH_2CH_2CH_2C}C(S)SCH_2N(C_2H_5)_2$ and $L'=CH_3N\overline{CCH_2CH_2CH_2C}C(S)SCH_3$



The alternate structure involving (II), appears to be much less probable due to the absence of discrete ν(C=C) and ν(C=N) vibrations which appear at considerably high energy range[4,5] *ca* 1650 cm^{-1}. In the metal complexes the bands of ν(C=N+C=S), ν(C=S+C=N) and ν(C=S) shift to lower frequency region[5-7] by 15-20 cm^{-1} suggesting invariably the bidentate behaviour of the esters. The characteristic bands of ν(C=C), ν(C=C+C=N) are observed at 1595±5 and 1360±5 cm^{-1} respectively[4,5]. The metal-nitrogen and metal-sulfur frequencies have been seen in the regions 450-525 and 325-400 cm^{-1} respectively[5-7].

The complexes of Ni(II) and Cd(II) are found to be diamagnetic whereas the complexes of Co(II) and Cu(II) are paramagnetic in nature with magnetic moments 2.12 and 1.90 B.M. respectively. On the basis of these results the complexes of Ni(II), Cd(II), Cu(II) and Co(II) are considered to have definite square-planar configurations. Fe(III) *tris* complex being octahedral[8] is found to have magnetic moments 5.35 B.M. which can also be taken as an additional evidence for the absence of S−S bonding in it arising out of the structure (II), since spin crossover behaviour[1] associated with S−S ligands decreases the magnetic moment to the order of 4.0 B.M. The somewhat lower magnetic moments in the Fe(III) complex in comparison to the usual high spin value (5.7−5.9 B.M.) can not be rationalized at the moment until the structure of the complex is determined by single crystal analysis. It may however be mentioned that the magnetic behaviour of the well characterized S−N chelates under octahedral environment is not known[1,8]. It is from this objective, that we have begun examining the structure of the Fe(III) complex by X-ray analysis.

The esters in their electronic spectra exhibit two or three bands in 25,000−39,000 cm^{-1} region (Table 2) due to intraligand transitions of the π-π^* type. The spectra (Table 2) of all the complexes are similar to each other in the ultraviolet region

where absorptions involving the ligands predominate. The bands in the region 24,000-45,000 cm^{-1} have been assigned as either M – L, L – M or ligand transitions[6,7]. The highly covalent character of the metal dònor bonds of the metal chelates is evidenced[6] by the dissimilarity between the spectra of the free esters and the metal chelates. The presence of the bands in the region 16,000-16,700 cm^{-1} assignable to MN_2S_2 chromophores (d-d) in the complexes of Ni(II)[6-7,9], Cu II)[6,10,11] and Co(II)[5,6,12] is strong evidence for the delocalization in the ring and also for their square-planar geometry. In Fe(III) octahedral complex a band at 11,525 cm^{-1} has been observed due to d-d transitions[6].

The complexes of diethylaminomethyl ester could not be scanned for pmr spectra due to poor solubility. The spectrum of the Ni(II) compound with the methyl ester exhibits a slight upfield shift[6,7] in the signals for SCH_2, 3,5-CH_3 and NCH_3 protons whereas 4 – CH_3 protons remain at the same position in comparison to the ligand[4]. Surprisingly, N-methyl protons appear as doublet (centred at 3.15 ppm) which defy interpretation except in terms of the two environmentally different positions of the methyl group with respect to the chelate ring.

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Preparation and Characterization of *Bis*-Dithiocarbamato di-*p*-Tolyl Tin(IV)

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Bis-Dithiocarbamato di-p-tolyltin(IV), i.e., $(p\text{-}CH_3C_6H_4)_2Sn(S_2CNRR')_2$ (where R=R'=CH_3, C_2H_5, i-C_3H_7; R=CH_3, C_2H_5, i-C_3H_7 and R'= $-C_6H_5$, $-CH_2C_6H_5$ or RR'=*morpholine*, 4-methylpiperidine and N-piperizine), were prepared by the reaction of di-p-tolyltin(IV) dicholoride with the sodium salt of respective dithiocarbamate acid in acetone medium in the stoichiometric ratio of 1 : 2

The compounds have been duly characterized on the basis of infrared and nmr spectroscopic data. Anisobidentate nature of dithiocarbamate moiety has been suggested in these compounds.

IN recent years a great deal of work has been reported on the synthesis and structural chemistry of organotin(IV) dithiocarbamates. The interesting aspect of organotin(IV) dithiocarbamates lies in the fact that unlike other metals or organometal dithiocarbamates, dithiocarbamate moiety in tin(IV) dithiocarbamates can be bonded to central tin atom either through one sulphur or both of the sulphur atoms of dithiocarbamate ligand.

Spectroscopic investigations including ir and uv spectral studies on various types of organotin(IV) dithiocarbamates suggest that in triorganotin(IV) dithiocarbamates $R_3Sn(S_2CNR'R'')$ or $RSnCl$-$(S_2CNR'R'')_2$, the ligand behaves as monodentate[1-3] whereas in diorganotin(IV) *bis* dithiocarbamates, the dtc ligand acts as bidentate moiety[4-9]. However, the crystallographic studies on $(CH_3)_2Sn(IV)$-$[S_2CN(CH_3)_2]_2$ show that dtc ligand is bonded to tin metal atom in an unsymmetrical fashion with two different Sn–S bond lengths i.e., 2.48 and 2.78 Å. This situation of one 'normal' and one 'weak' Sn–S bond lengths is consistent with the result obtained using Mossbauer spectroscopy[11] and has led to the coining of the term "anisobidentate" nature of these ligands in these tin(IV) compounds.

The present work deals with the synthesis of new *bis* disubstituted dithiocarbamato-di-*p*-tolyltin(IV) of the type, $(p\text{-}CH_3C_6H_4)_2Sn(S_2CNRR')_2$ (where R=R'=CH_3, C_2H_5, i-C_3H_7; R=CH_3, C_2H_5, i-C_3H_7, R'=C_6H_5, $-CH_2C_6H_5$ or RR'= morpholine, 4-methylpiperidine, N-methylpiperizine) and characterisation of these with the help of ir and nmr spectral studies.

Experimental

Sodium salts of N,N-disubstituted dithiocarbamic acid of the type NaS_2CNRR' (where R=R'=CH_3, C_2H_5, i-C_3H_7; R=CH_3, C_2H_5, i-C_3H_7, R'=$CH_2C_6H_5$, C_6H_5; RR'=morpholine, 4-methylpiperidine, N-methyl piperizine) were prepared in good yield in aqueous solution by the reaction of an appropriate secondary amine, carbon disulphide and sodium hydroxide as described by Klopping *et al*[12]. Since the salts contain water of crystallization they were dried first in vacuum over P_4O_{10} at room temperature and then at 110° until their spectra showed no trace of water.

Tetra-*p*-tolyltinIV was prepared by Wurtz reaction, using a mixture of *p*-chlorotoluene (50.6 gm; 0.4 mol), sodium metal (18.4 gm; 0.8 mol) and tin tetrachloride (26.6 gm; 0.1 mol) in hydrocarbon solvents[13].

Di-*p*-tolyltin(IV) dichloride was prepared by disproportion reaction of tetra-*p*-tolyltin(IV) and tin tetrachloride.

Bis-*N,N-dimethyldithiocarbamato-di-p-tolyltin(IV)*: To a solution of di-*p*-tolyltin dichloride (0.371 gm; 0.001 mol) in dry acetone (60 ml) was added with constant stirring, a solution of sodium salt of N,N-dimethyldithiocarbamate (0.286 gm; 0.002 mol). The mixture was refluxed for half an hour and then kept at room temperature for half an hour and filtered. The filtrate was evaporated under vacuum to give a yellow solid. The yellow solid upon recrystallization from dichloromethane and petroleum ether gave a light yellow solid corresponding to the formula $(p\text{-}CH_3C_6H_4)_2Sn$-$[S_2CN(CH_3)_2]_2$ with 80% yield, m. p. 137°.

Similarly, *bis*-dialkyldithiocarbate-*p*-tolyltin(IV), viz., N,N-di-isopropyl, N,N-methyl phenyl, N,N-methyl benzyl, N,N-ethyl benzyl, N-methylpiperizine, 4-methylpiperidine and morpholine dithiocarbamato di-*p*-tolyltin(IV) complexes were prepared.

Analytical data of the complexes are given in Tables 1 and 2.

anisobidentate group in these complexes as *bis*-tolyl *bis* dimethyl dithiocarbamatotin(IV) compound (I) shows. The resonance signals due to $-CH_3$ protons in this complex appears at 6.6 τ. This value is intermediate between monodentate and pure bidentate[29] dithiocarbamate complexes and corresponds very well to the analogous *bis* alkyl *bis* dithiocarbamatotin(IV) complexes[4]. It should be noted, however, that these data refer to solution species.

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Polarographic Study of Ternary Complexes in Solution : Complex Formation Between Copper(II) 2,2'-bipyridyl 1 : 1 Complex and Ligands Containing Oxygen and/or Nitrogen Donor Atoms as Secondary Ligands

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Electrode behaviour of some mixed-ligand complexes of Cu(II) with 2,2'-bipyridyl as primary ligand and some aliphatic, aromatic and amino acids and phenols as secondary ligands have been studied in aqueous potassium nitrate. All the complexes are observed to undergo diffusion controlled, single-step, two electron irreversible electro-reduction at dme. The study has been made at three different temperatures namely 30, 35 and 40° and at the varying ratio of 1 : 1 : 1 and 1 : 2 : 1 for the metal : (primary ligand) : (secondary ligand). Besides half wave potentials, $E_{1/2}$ the formal rate constant, k_f, the activation energy of rearrangement of the depolarizer, Q_r, the activation energy of diffusion, Q_D have been calculated for each system. It is observed that all the complexes follow a particular reaction mechanism with temperature and the half-wave potential shifts towards more positive side with rise of temperature indicating easier reduction, with the exception of the complexes with aromatic acids and catechol. Factors for this behaviour have been observed. The driving forces for the formation of ternary systems have been analysed. Discriminating nature of the parent 2,2'-bipyridyl complex towards incoming secondary ligands has been discussed.

THE present heightened interest in the solution chemistry of ternary complexes[1-7] of biologically important metal ions stems out of the consideration that mixed chelation occurs commonly in biological fluids as a large variety of potential ligands are likely to compete for metal ions found *in vivo*[8]. It is well known that ternary complexes play an important role in biological process. Ternary complexes containing Cu(II)[9-11] as a metal ion are relatively well investigated because copper is a very important element essential to the healthy life of plants[12-15] and animals[16-19].

Many potentiometric determinations during the last decade have been directed to reveal driving forces of the ternary complexes giving importance to electronic effects (π systems of the ligands) besides coulombic effects (neutralization of charge in ternary complexes) and lower steric hindrance compared with corresponding binary *bis*-complexes[20]. A general impression appears to have gained ground that these mixed-ligand complexes would be more stable than one would expect for purely statistical reasons. Sigel and coworkers have further been able to hint at the discriminating qualities of Cu^{2+}-2,2'-bipyridyl, 1 : 1 complex towards the second ligand to be coordinated. Polarographic studies, though expected to furnish more exact information on factors like electronic effects, have been used much less due to obvious difficulties in applying the technique to these systems.

Considering that the electrode behaviour is a characteristic property of coordination compounds[21] and further considering that the dynamic character of polarography has been used in recent years[22] to express the reactivity and kinetic properties of such compounds, the present study is an attempt to gather facts leading to a better understanding[23] of the electrode behaviour of these ternary complexes at the dropping mercury electrode in general.

The system chosen for the present study involves 2, 2'-bipyridyl as a primary ligand and a number of O or O ; N and N donors. All the polarographic characteristics have been determined under the assumption that the complex formation between Cu^{2+}-2,2'-bipyridyl-ligand is complete. This assumption is reasonable and it is confirmed by Sigel[20]. The secondary ligands taken for study are : ethylenediamine (en), $NH_2CH_2CH_2NH_2$, a N-donor, amino acids [glycine (Gly) NH_2CH_2COOH, valine (Val) $(CH_3)_2$ CH CH NH_2COOH, serine (Ser) HO $CH_2CH(NH_2)$ COOH, leucine (Leu) $(CH_3)_2$ CH CH_2CH (NH_2) COOH] all N-O donors, aliphatic acids [formic acid (For) HCOOH, oxalic acid (Ox) $(COOH)_2$, tartaric acid (Tar) (CH OH $COOH)_2$, citric acid (Cit) $(CH_2COOH)_2$ C(OH) COOH, succinic anid (Suc) $(CH_2COOH)_2$] aromatic acids [benzoic acid (Ben) C_6H_5COOH, phthalic acid (Ph) $C_6H_4(COOH)_2$, salicylic acid (Sal) C_6H_4OH COOH, mandelic acid (Man) $C_6H_4(CHOH)_2$, gallic acid (Gal) $C_6H_2(OH)_3COOH$] and phenols

[resorcinol (Res) $C_6H_4(OH)_2$, catechol (Cat) $C_6H_4(OH)_2$] all O – donors.

Experimental

All studies were made in double-distilled water and fresh solutions of the ligands were prepared when needed. All chemicals used were of AnalaR grade. Twenty ml of reaction mixture (depolarizer + supporting electrolyte + maximum supressor + solvent) were always taken in the polarographic cell, care being taken to keep the supporting electrolyte concentration constant. Polarographic measurements were made with a manual polarographic circuit recommended by Kolthoff and Lingane[24]. All potentials were measured against a Hume and Harris saturated calomel electrode (SCE). Other experimental details have been described elsewhere[25]. Resistance of the system was measured by an ac wheatstone bridge. The resistance was found to be between 700-800 Ω.

The characteristics of the dropping mercury electrode (open circuit) were determined for at least three heights. One such set is given below

$h = 30$ cm, $m = 1.85$ mgs^{-1}, $t = 4.1$ sec.
$m^{2/3} = t^{1/6} = 1.877$ mg$^{2/3}$ s$^{-1/2}$

The systems studied are [Cu(bip)L] in the ratios 1 : 1 : 1 and 1 : 2 : 1 at temperatures 30, 35 and 40°.

Results

Tables 1 and 2 contain the polarographic characteristics of the system [Cu(bip)L] in the ratios of 1 : 1 : 1 and 1 : 2 : 1 in 0.5*M* KNO_3 aqueous solution. The morphology of curves show single well-defined waves at dme for all the cases except in the cases [Cu(bip)Gal], [Cu(bip)Leu] and [Cu(bip)Cat], in which two step reduction wave is obtained. Perusal of the $E_{\frac{1}{2}}$ values for these systems lead to the conclusion that [Cu(bip)] 1 : 1 and 1 : 2 binary complex is difficult to reduce than the ternary aliphatic and aromatic acids complexes except the complex [Cu(bip)Ox] and [Cu(bip)Ben] but the ternary complexes of amino acids are more stable. The values of formal rate constants also support the same results. The slope values calculated by the "log-plot" (Oldhan and Parry) E vs log (5.5 – x) x/5 (1 – x) indicate that all the complexes undergo irreversible electro-reduction in aqueous solution as the values of the slope are greater in each case than the theoretical value of 0.029 v. The values of half-wave potentials $E_{\frac{1}{2}}$ are also calculated by the 'log-plot' given above. The value of number of electrons transferred 'n' calculated by Ilkovic equation was nearly equal to two for each of the complexes except in case of complexes involving gallic acid, leucine and catechol in which the value of 'n' is about one for both waves. Values of diffusion current i_d(μa) are directly taken from the polarographic waves. Formal potentials have been determined experimentally vs SCE. Rate constants (K_f) are calculated with the help of formal potential. The diffusion controlled nature of the polarographic waves was determined by varying the height of mercury column and studying the corresponding change in diffusion currents. The constancy of $i_d/h^{\frac{1}{2}}_{eff}$

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF MIXED LIGAND COMPLEXES OF Cu(II) (1 . 1 : 1)

h = 40 cm   Temp 35° KNO_3 = 0.5*M*

Complex	$E_{\frac{1}{2}}$ Volt vs SCE	Slope (Volts)	Diffusion current i_d (μa)	Transfer coefficient 'α'	Diffusion coefficient 'D' cm²/sec 1 × 10⁻⁶	Formal potential vs SCE at 35°	Formal rate constant 'K_f' cm sec⁻¹ 1 × 10⁻⁴
Cu bip	– 0 1065	0.0720	0 6540	0 3900	0 0549 × 10⁻¹	+ 0.020	0.1557 × 10⁻¹
Cu : bip : For	– 0.0980	0 1050	1.0100	0 2682	0.1309	– 0.056	1.6420
Cu : bip · Ox	– 0.1100	0 1800	1.2400	0.1667	0 1973	– 0.048	1.5620
Cu : bip · Tar	– 0.0970	0.0930	1.0000	0.2565	0 1309	– 0.064	1.6720
Cu : bip Cit	– 0 0920	0.1150	1.1000	0.2269	0.1539	– 0.069	1.7950
Cu : bip : Suc	– 0.0920	0.1260	1.0800	0.2341	0.1497	– 0.068	1.7480
Cu bip · Ben	– 0.1100	0 1510	1.0100	0 1821	0 1309	– 0 050	1.4080
Cu , bip : Ph	– 0 1000	0.1410	1.0500	0 2034	0 1416	– 0 060	1.5760
Cu : bip : Sal	– 0.0880	0.0920	1.0000	0 2950	0.1237	– 0.047	1.6460
Cu : bip : Man	– 0 0900	0.1030	1.0200	0 2680	0 1054	– 0.072	1.5660
Cu : bip · Gal	– 0.0530	0.0720	0.6700	0 3990	0 0576 × 10⁻¹	– 0.054	1 1180
	– 0 2800	0 0620	0.2600	0.4610	0 0086 × 10⁻¹		0.2680 × 10⁻¹
Cu : bip : Gly	– 0 1070	0.1670	1.0600	0.1799	0 1442	– 0.081	1.4160
Cu : bip : Val	– 0.1490	0.2800	1.1600	0.0925	0.1728	– 0 048	1.0100
Cu : bip : Ser	– 0.1150	0.1450	1.0800	0.1639	0.1497	– 0.064	1.4580
Cu : bip Leu	– 0.0105	0.0270	0.5100	2.0840	0.0833 × 10⁻¹		1.1820
	– 0.3150	0 1410	0.5000	0.5320	0 0326 × 10⁻¹	– 0.0385	0.4786 × 10⁻¹
Cu : bip . Res	– 0.0975	0.1370	0.0900	0.2100	0.2416	– 0.095	1.9950
Cu · bip · Cat	– 0.0880	0 0750	0.6700	0.7400	0.0576		1.0580
	– 0.3880	0.0830	0.2900	0.7000	0.0107 × 10⁻¹	– 0.0	0.2270 × 10⁻¹
Cu : bip : En	– 0.1068	0.2670	1.5500	0.2284	0.3083	– 0.06	1.421

TABLE 3—POLAROGRAPHIC CHARACTERISTICS OF MIXED LIGAND COMPLEXES OF Cu(II) (1 : 2 : 1)

h=40 cm Temp.=35° KNO_3 =0.5M

Complex	$E_{\frac{1}{2}}$ Volt vs SCE	Slope (Volts)	Diffusion current i_d (μa)	Transfer coefficient 'α'	Diffusion coefficient 'D' cm^2/sec 1×10^{-6}	Formal potential vs SCE at 35°	Formal rate constant 'K_f' $cm\ sec^{-1}$ 1×10^{-4}
Cu : bip	−0.2000	0.2680	1.1100	0.1070	0.1558	−0.065	0.5679×10^{-1}
Cu : bip : For	−0.1420	0.0890	0.8900	0.3162	0.1016	−0.095	1.5080
Cu : bip : Ox	−0.2000	0.2000	1.0000	0.1329	0.1283	−0.100	1.0920
Cu : bip : Tar	−0.1780	0.1150	0.7800	0.2611	0.0515×10^{-1}	−0.100	3.0310
Cu : bip : Cit	−0.1600	0.1180	1.0000	0.1109	0.1288	−0.125	1.1530
Cu : bip : Suc	−0.1620	0.1310	1.0000	0.1756	0.1288	−0.100	1.3850
Cu : bip : Ben	−0.2000	0.2800	0.7200	0.0988	0.0665×10^{-1}	−0.150	0.7621×10^{-1}
Cu : bip : Ph	−0.1600	0.1140	0.9100	0.2860	0.1068	−0.101	1.3780
Cu : bip . Sal	−0.1860	0.1000	0.8200	0.3010	0.1086	−0.101	1.5730
Cu : bip : Man	−0.1440	0.0860	0.9200	0.2810	0.0868×10^{-1}	−0.133	4.5900
Cu : bip : Gal	−0.2120	0.1800	0.9820	0.2660	0.1594	−0.125	1 0860
Cu : bip : Gly	−0.2570	0.1920	1.0100	0.1879	0.1309	−0.145	1.1140
Cu : bip : Val	−0.2650	0.1850	1.0300	0.1695	0.1809	−0.169	1.2620
Cu : bip : Ser	−0.2600	0.1450	1 0100	0.1998	0.1361	−0.108	1.1680
Cu : bip : Leu	−0.2420	0 2150	1 0600	0.1245	0 1442	−0.162	1.1690
Cu : bip : Res	−0.1840	0.1600	1.0800	0.1800	0.1497	−0.134	1 5320
Cu : bip : Cat	−0.1100 } −0.4050 }	0.0600 } 0.0670 }	0.4400 } 0.3600 }	0.9200 } 0.7300 }	0.0248×10^{-2} } 0.0166×10^{-1} }	−0.133	0.9298×10^{-2} } 0.3710×10^{-2} }
Cu : bip : En	−0.2210	0.2000	1 5500	0.2990	0.3083	0.060	1.4210

values show that the process is diffusion controlled. Higher values of diffusion currents, i_d in case of ternary complexes are observed in comparison to the binary [Cu(bip)] 1 1 and 1 2 system, because the chelation makes the depolarizer smaller than [Cu(bip)] complex Amongst the chelates so formed, the ternary complexes of oxalic acid, benzoic acid and valine are smaller than those of the other acids and provide the highest value of diffusion current in each series The observed values of diffusion coefficients 'D' support this argument The values of $E_{\frac{1}{2}}$ for the complexes are given in Tables 1 and 2.

The activation energy, Q_a, and the activation energy of the diffusion, Q_D, have been calculated using the following given by Vlček[26].

$$\log \frac{i_d - i}{i} = -\log A' + \frac{Q_a - \frac{1}{2}Q_D}{2.3\ RT} \qquad (1)$$

$$\text{and}\ \log \frac{i_d}{m^{2/3}t^{1/6}} = \log 0.67\ n\ F\ CD_{\frac{1}{2}} - \frac{\frac{1}{2}Q_D}{2.3\ RT} \qquad (2)$$

where symbols have their usual meanings. The data on activation energy of diffusion and rearrangement of the Cu(II) bip complexes [Cu(bip)L] with secondary ligands are given in Table 4 The plots of half-wave potential vs temperature (Figs. 1-4) are found to be straight lines. It may therefore be concluded[27] that the electroreduction of these complexes follows a particular reaction mechanism with temperature. It has been observed that for all the complexes, the value of diffusion current i_d increases and that of half wave potential $E_{\frac{1}{2}}$ shifts towards more positive values with the increase of temperature indicating easier reduction[28,29]. However in the case of [Cu(bip)cat], [Cu(bip) aromatic acids[1], the $E_{\frac{1}{2}}$ values become more negative with the rise of temperature. This is probably because of decreased adsorption of catechol and aromatic acids at higher temperature (Figs. 5a and b). The current potential curves for these complexes are well-defined waves at all temperatures (30, 35, 40°). The diffusion current values for all these complexes increase with the rise in temperature. The transfer coefficient α increases with temperature indicating that the electroreduction process becomes more and more reversible at higher temperature (Table 3). The values of activation energy increase within the series with increase in the value of half-wave potential. The activation energy of [Cu(bip)cat] 1 : 1 : 1 cannot be calculated because the dependence of $i_d - i/i$ vs T^{-1} is not linear due to its adsorption nature. Such a behaviour indicates complicated course of the electrode reaction[30].

TABLE 4—ACTIVATION ENERGY 'Q_a' AND ACTIVATION ENERGY OF DIFFUSION 'Q_D' OF Cu(II)BIPYRIDYL MIXED LIGAND COMPLEXES

Complexes	1 : 1 : 1		1 : 2 : 1	
	$Q_D(K_{cal})$	$Q_a(K_{cal})$	$Q_D(K_{cal})$	$Q_a(K_{cal})$
Cu bip	3.2575	6 7780	7.8824	10.2100
Cu : bip Form	2.3257	5 8230	7 0034	9.2164
Cu . bip . Ox	3 8221	6 2751	7 3210	10.1275
Cu bip Tar	1 8474	5 5200	6 8080	8.0040
Cu bip Cit	1 7423	5.5620	6.5670	7.8766
Cu · bip Suc	1.5253	5 5525	6.1240	7.7777
Cu : bip : Ben	3.2810	7.1280	9.5280	11.2851
Cu . bip Ph	2.1436	6 7276	9 2000	10.7180
Cu . bip Sal	1.5232	5 7034	8 7200	10.2165
Cu bip . Man	1.8236	5.7100	8.5120	9.2375
Cu . bip Gal	2.3236	5.8284	6 2810	9.0201
Cu : bip Gly	6 8	9.7980	9.2	12.2820
Cu . bip . Ser	7.8	9 8800	9 7	12.5670
Cu . bip . Val	8 5	10 2845	9.8	13.2620
Cu : bip : Leu	6.65	8.6285	8.5	11.2610
Cu : bip . Res	2 102	5.7852	6.9278	10.8006
Cu : bip : Cat	—	—	7.6231	10.8752
Cu . bip . En	9 752	23.276	10.285	25.2100

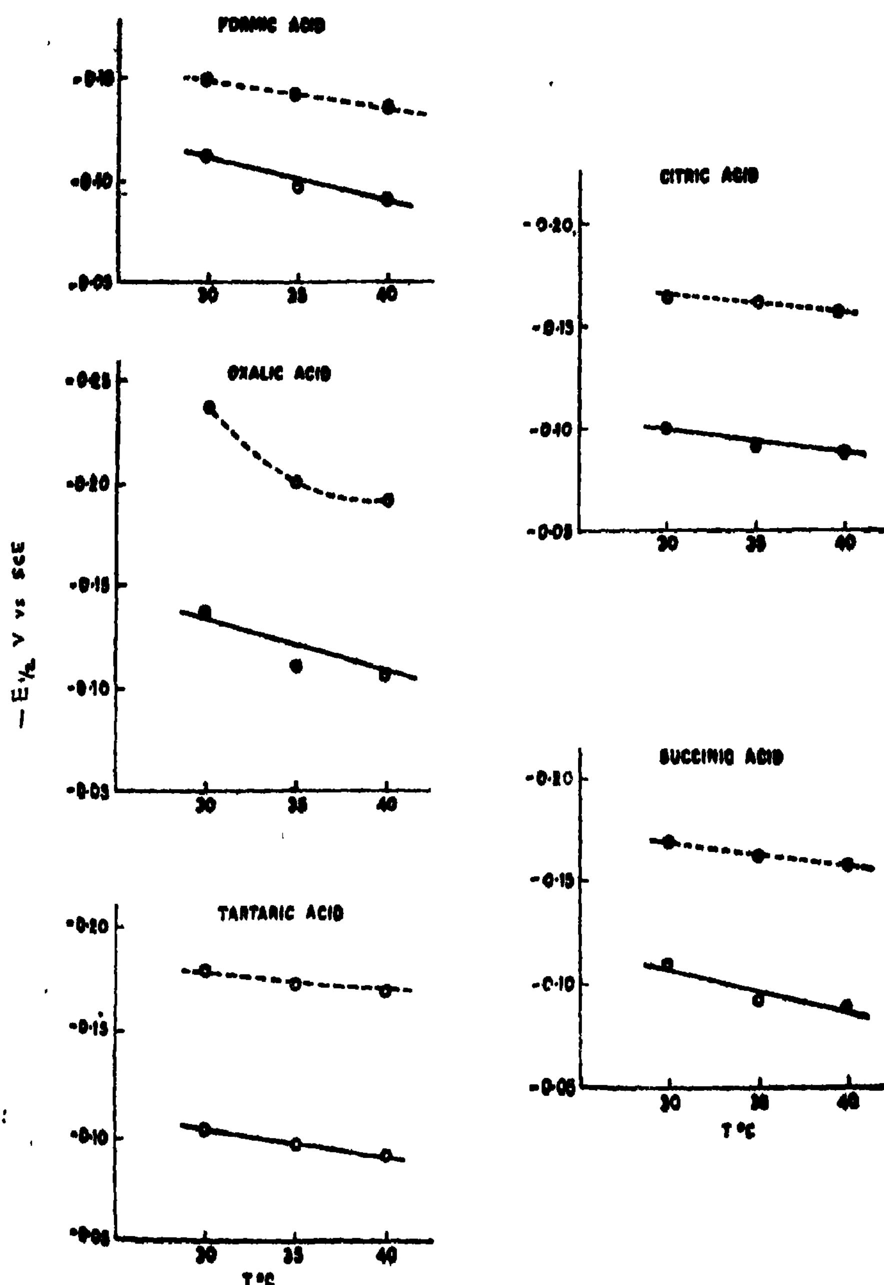


Fig. 1. Effect of temperature on half wave potential of Cu bip aliphatic acids (1 : 1 . 1 ——) (1 . 2 . 1 - - - - - -).

iscussion

Among the mixed-ligand complexes of aliphatic :ids series, the complex, [Cu(bip)Ox], seems to be ie most stable in comparison with others. There 'e several factors governing the stability of a mplex, whether simple or mixed, like statistical ctors, geometry of the mixed complex, steric ctors (size of the ligand), size and charge on metal n, charge on ligands, etc. All the factors being e same, the stability of the mixed-ligand complexes in this series can be expected to follow the order of size of the secondary ligand, namely oxalic acid < tartaric acid < succinic acid < citric acid. The complex involving a monodentate and less charged ligand like formic acid should be less stable than other complexes of the series. In the series [Cu(bip) aromatic acids], the complex [Cu(bip) Ben] seems to be the most stable. Benzoic acid has the smallest size in the series, but it is also a monodentate ligand. However, the presence of the aromatic ring[20,21] alters bonding properties of this

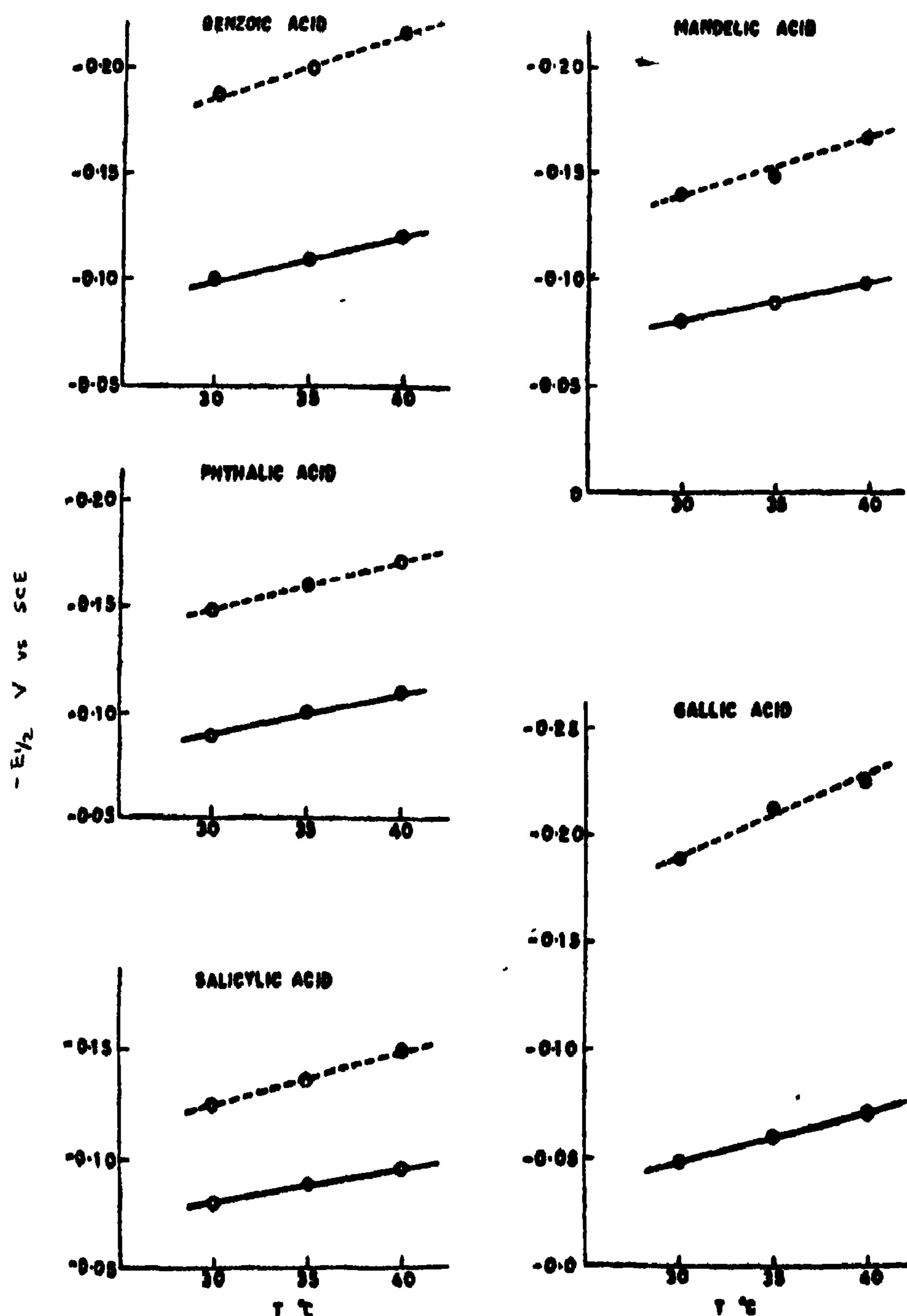


Fig. 2. Effect of temperature on half wave potential of Cu : bip : aromatic acids (1 : 1 : 1 ——) (1 : 2 : 1 --- ---)

carboxylic acid if compared with the formic acid. Among complexes involving amino acids as secondary ligands the [Cu(bip) Val] complex is the most stable. The half-wave potentials shift towards more negative values in the series [Cu(bip)Gly] < [Cu(bip)Ser] < [Cu(bip)Val] and the rate constant decreases. This means that the ease of reduction decreases or the rate of electron transfer decreases in this series of complexes. Available stability constant data also support the same trend[22,23]. In the series the stability constant being highest for the complex [Cu(bip)Val] which may indicate[21,24-27] that here the electron density around the central metal ion is also comparatively high and this would render acceptance of the two incoming electrons

TABLE 3—POLAROGRAPHIC CHARACTERISTICS OF Cu(II)-BIPYRIDYL MIXED LIGAND COMPLEXES AT DIFFERENT TEMPERATURES

Complexes	T°C	h=40 cm 1:1:1 $E_{\frac{1}{2}}$ (V vs SCE)	i_d (μa)	α	KNO_3=0.5M 1:2:1 $E_{\frac{1}{2}}$ (V vs SCE)	i_d (μa)	α
Cu : bip : For	30	−0.1115	0.9840	0 2602	−0.1488	0.8090	0.3222
	35	−0.0980	1.0100	0.2632	−0.1490	0.8900	0.3162
	40	−0.0955	1.1100	0.2730	−0.1882	0.9520	0.3070
Cu : bip : Ox	30	−0.1872	1.2000	0.1532	−0.2375	0.9726	0.1462
	35	−0 1100	1.2400	0.1667	−0.2000	1.0000	0.1829
	40	−0.1070	1.3120	0.1720	−0.1925	1.0856	0.1998
Cu : bip : Tar	30	−0.1050	0.9950	0.2201	−0.1805	0.6950	0.2707
	35	−0.0970	1.0000	0.2565	−0.1730	0.7800	0.2611
	40	−0.0925	1.0922	0.2628	−0.1710	0.8920	0.2589
Cu : bip : Cit	30	−0.1000	0.9870	0.2129	−0.1685	0.9620	0.1112
	35	−0.0920	1.0000	0.2269	−0.1600	1.0000	0.1109
	40	−0.0900	1.1200	0.2369	−0.1585	1.1213	0.1000
Cu : bip : Suc	30	−0.1100	0.9950	0.2212	−0.1685	0.9821	0.1820
	35	−0.0920	1.0800	0.2341	−0.1620	1.0000	0.1756
	40	−0.0890	1.1022	0.2398	−0.1575	1.0999	0.1725
Cu : bip : Ben	30	−0.1004	0.0100	0.1803	−0.1885	0.7115	0.0980
	35	−0.1100	0.0100	0.1821	−0.2000	0.7200	0.0988
	40	−0.1222	0.0832	0.1870	−0.2175	0.7396	1.0232
Cu : bip : Ph	30	−0.0904	1.0820	0.2005	−0.1475	0.8700	0.2250
	35	−0.1000	1.0500	0.2084	−0.1600	0.9100	0.2380
	40	−0.1098	1.0778	0.2124	−0.1720	0.9445	0.2389
Cu : bip : Sal	30	−0.0802	0.0982	0.2910	−0.1250	0.8175	0.2820
	35	−0.0880	1.0000	0.2950	−0.1360	0.8200	0.3010
	40	−0.0952	1.0555	0.2975	−0.1487	0 8240	0.3120
Cu : bip : Man	30	−0.0820	1.0022	0.2635	−0.1415	0.9155	0.2775
	35	−0.0900	1.0200	0.2680	−0.1500	0.9200	0.2810
	40	−0.1005	1.0532	0.2705	−0.1685	0.9285	0.2890
Cu : bip : Gal	30	−0.0480	0.6625	0.3982	−0.1898	0.8120	0.2600
		−0.2790	0.2585	0.4690			
	35	−0.0590	0.6700	0 3990	−0.2120	0 8970	0.2660
		−0.2800	0.2600	0.4610			
	40	−0.0715	0.6780	0.3998	−0.2145	0.9395	0.2715
		−0.2825	0 2625	0.4600			
Cu : bip : Gly	30	−0.1200	1.0050	0 1742	−0.2789	1.0025	0.1285
	35	−0.1070	1.0600	0.1799	−0.2570	1 0100	0 1379
	40	−0.0825	1.1011	0.1822	−0.2355	1 0225	0.1394
Cu : bip : Ser	30	−0.1295	1.0832	0.1615	−0.2825	1.0075	0.1973
	35	−0.1150	1.0800	0 1689	−0.2600	1.0100	0.1993
	40	−0.1015	1.1000	0.1664	−0.2385	1.0375	0 2015
Cu : bip : Val	30	−0.1615	1.1025	0.0910	−0.2875	1.0225	0.1545
	35	−0.1490	1.1600	0.0925	−0.2650	1.0800	0 1595
	40	−0.1400	1.1885	0.1200	−0.2600	1.0875	0.1615
Cu : bip : Leu	30	−0.0080	0.5050	2.0000	−0.2580	1.0553	0.1200
		−0.3575	0.4920	0.5420			
	35	−0.0105	0.5100	2.0340	−0.2420	1.0600	0.1245
		−0.3150	0.5000	0.5320			
	40	−0.0118	0.5150	2.2525	−0.2200	1.0985	0.1273
		−0.2988	0.5120	0.5315			
Cu : bip : Res	30	−0.0992	1.0775	0.2000	−0.1875	1.0582	0.1695
	35	−0.0975	1.0900	0.2100	−0.1840	1.0800	0.1800
	40	−0.0890	1.2700	0.2400	−0.1800	1.1082	0.1825
Cu : bip : Cal	30	−0.0915	0.6000	0.7332	−0.1085	0.4225	0.9117
		−0.3775	0.2815	0.7225	−0.4000	0.3515	0.7375
	35	−0.0880	0.6700	0.7400	−0.1100	0.4400	0.9200
		−0.3880	0.2900	0.7000	−0.4050	0.3600	0.7300
	40	−0.0825	0.6975	0.7495	−0.1135	0.4475	0.9265
		−0.3915	0.3085	0.6925	−0.4115	0.3675	0.7289
Cu : bip : En	30	−0.2000	1.29	0.2170	−0.2070	1.2900	0.2684
	35	−0.1068	1.55	0.2284	−0.2210	1.5500	0.2990
	40	−0.1060	1.60	0.2637	−0.2530	1.6000	0.2950

TABLE 5—HALF WAVE POTENTIALS OF Cu : bip : AMINO ACIDS (O AND N DONOR) AND Cu : bip : ETHYLENEDIAMINE (N DONOR LIGAND) ; Cu : bip : ALIPHATIC ACIDS (OXYGEN DONOR) ; Cu : bip : AROMATIC ACIDS (OXYGEN DONOR) AND Cu : bip : PHENOLS (OXYGEN DONOR)

$-E_{\frac{1}{2}}$ of Cu ; bip (1 : 1)=0 1065

Secondary Ligands	I $-E_{\frac{1}{2}}$ CuL	II $-E_{\frac{1}{2}}$ Cu(bip)L	III [Cu(bip)L]-[Cubip]	IV [Cu(bip)L]-[CuL]	V [{Cu(bip)L-Cu(bip)}-CuL] $\Delta E_{\frac{1}{2}}$
Cu : bip · Amino Acids (O and N donor) and Cu : bip : ethylenediamine (N donor ligand)					
Ethylenediamine	−0.02	−0.1068	−0.0080	−0 0868	+0.027
Glycine	+0 005	−0.1070	−0.0005	−0.1020	−0 0045
Valine	+0.028	−0.1490	−0.0425	−0.1210	−0.0145
Serine	+0.017	−0.1150	−0.0085	−0.1080	0 0085
Leucine	−0.20	−0.3150	−0.2085	−0.1150	−0.0085
Cu : bip : Aliphatic Acids (Oxygen donor)					
Formic acid	+0.020	−0.098	+0.0035	−0.078	−0.0115
Oxalic acid	+0 015	−0.110	+0 0095	−0 095	−0 0115
Tartaric acid	+0 020	−0.097	+0 0095	−0.077	−0.0105
Citric acid	+0.025	−0 092	+0.0145	−0.067	−0.0105
Succinic acid	+0 027	−0.032	+0.0145	−0.066	−0.0115
Cu : bip : Aromatic Acids (Oxygen donor)					
Benzoic acid	+0.018	−0.1100	−0.0035	−0 092	−0.0145
Phthalic acid	+0.022	−0.1000	+0.0065	−0 078	−0 0155
Salicylic acid	+0.080	−0.0880	+0.0185	−0.0580	−0.0115
Mandelic acid	+0.028	−0.0900	+0.0165	−0.0620	−0.0115
Gallic acid	+0.020	−0.0535	−0.0530	−0.0835	−0.0880
Cu · bip : Phenols (Oxygen donor)					
Resorcinol	+0 020	−0.0975	+0.0090	−0 0775	−0.0110
Catechol	− 0.270	−0.3880	−0.2815	−0.1180	−0.0115

depolarizer at the electrode surface and increased rate of charge transfer. Data on activation energy show that it decreases with decrease of half-wave potential indicating an easier reduction. Reduction is regarded as comprising the acceptance of an electron into the lowest unoccupied, or singly occupied orbital of the depolarizer. If the orbital has a high electron affinity, a slight change in configuration will take place for the direct reaction of the depolarizer particle with electrode. A large amount of energy of rearrangement will be necessary if the orbital has a low electron affinity since direct reduction in this instance would require a very large negative applied potential, so the activation energy is proportional to the half-wave potential of the complexes.

To observe the discriminating power of 2,2'-bipyridyl complex towards various secondary ligands the effects of different ligands competing in the complex formation and the shift of $E_{\frac{1}{2}}$ values have been separated by taking the difference of $E_{\frac{1}{2}}$ for [Cu(bip)L] and [CuL], the $\Delta E_{\frac{1}{2}}$, [{Cu(bip)L − Cu(bip)} − (CuL)] being calculated as difference of the values of column III and I of Table 5.

For the 2,2' bip-Cu^{2+} − en system, a positive $\Delta E_{\frac{1}{2}}$ value is observed. In agreement with the results the value of $\Delta E_{\frac{1}{2}}$ for the mixed O, N ligand, i.e. amino acids, the values are in between those found for O, O and N ligand. The observation of a positive $\Delta E_{\frac{1}{2}}$ value would mean that the ligai under consideration forms a more stable compl with the free (hydrated) Cu^{2+} ion than with t Cu^{2+} − 2,2' bip 1 : 1 complex. However it does n mean that no ternary complex is formed in solutio containing equimolar mixtures of two differe ligands and Cu^{2+}. Thus Cu^{2+} − 2,2'-bip 1 : 1 compl seems to possess discriminating qualities towar other ligands, preferably coordinating 'O' containi ligand and the resulting ternary complexes bei remarkably stable. The ligand 2,2'-bipyrid induces a stronger field at the Cu^{2+} ion and it bound to Cu^{2+} through a donor bond but it is al a π acceptor (π bonds : back donation), hence t resulting charge on the Cu^{2+} ion in the 1 : complex is higher with 2,2'-bipyridyl. Thus distort octahedral $Cu(H_2O)_6{}^{2+}$ ion will be somewhat mo strongly distorted towards a square-planar coordin tion sphere by the coordination of 2,2'-bip., creati the right geometry for the coordination of t second ligand, which will be especially favour due to negatively charged donor oxygen atom Also the π system of the O-ligand seems also have some (but a smaller) effect. This sugge that in complexes like 2,2'-bip-Cu^{2+} − phenols, cooperative effect may occur between the π syste of the two ligands bound to the same Cu^{2+}. line with this assumption are results obtained f several ternary 2,2'-bip-Cu^{2+} − carboxylate co plexes. The aromatic acid anions form somewh more stable complexes with the Cu^{2+} − 2,2'-bip 1 : complex than aliphatic carboxylic acid anions[48].

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Organophosphonic Acids as Complexones Part—II : Interaction of Ethylenediphosphonic Acid with Some Divalent Metal Ions

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Reactions between bivalent metal ions [Mn(II), Ni(II), Zn(II), Cd(II) and Pb(II)] and ethylenediphosphonic acid (EDP) have been carried out in aqueous medium and the solid products, $M_2L.nH_2O$ (n=0, 3 or 4), have been characterized on the basis of elemental analysis, ir and electronic spectral and magnetic measurement data. Thermal stability of the compounds has also been studied.

PREPARATION of ethylenediphosphonic acid (EDP) from ethylene glycol and phosphorus trichloride has been reported[1]. From the survey of the literature, it seems that no attempt has been made to use it as a complexing agent. In continuation of our work on organophosphonic acids[2], we report here the synthesis and structural studies of metal derivatives of ethylenediphosphonic acid. In the present investigation, reactions with bivalent metals, Mn(II), Ni(II), Zn(II), Cd(II) and Pb(II), have been studied.

Experimental

Phosphorus trichloride and ethyleneglycol (B. D. H.) and bivalent metal acetates (B. D. H., AnalaR) were used as such.

Preparation of the ligand · *Bis* (ethylene) dihydrogenphosphite was prepared by the method of Cook *et al*[3]. It was then hydrolysed by adding calculated amount of water to give EDP. The product was purified by distilling it under reduced pressure (Found : P, 31.9, $C_2H_8P_2O_6$ requires P, 32.63%).

Preparation of metal derivatives : Aqueous solution of the acid (1 mole) was added to metal salt solution (2 mole) with constant stirring at room temperature. The precipitation was effected by dropwise addition of dilute ammonia solution. The precipitates were filtered and washed with distilled water and then dried at 50-60° till constant weight They were neither soluble in water nor in any common organic solvent. They did not melt when heated even upto 300°. Elemental analysis using conventional methods[4], and colour of the compounds have been given in Table 1.

IR spectra were taken in nujol (600-4000 cm^{-1}) using KBr pellets on Beckman IR-20 spectrophotometer. Diffuse reflectance spectra in the region 200-1200 nm were run on a Unicam SP-700 spectrophotometer with a standard reflectance accessory using MgO as the reference. Magnetic measurements were made on Guoy's balance.

TABLE 1—PHYSICAL STATE, ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA

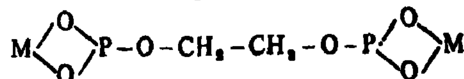
Compound	Colour and state	Analysis %M		Analysis %P		μ_{eff} B.M.
		Found	Calcd.	Found	Calcd.	
Mn_2EDP	White solid	37 4	37 1	20.9	20.9	3.85
$Ni_2EDP.4H_2O$	Light green solid	30 9	31 2	16.18	16.30	2.24
$Zn_2EDP.3H_2O$	White solid	34 06	34 9	15 00	16.7	—
$Cd_2EDP.3H_2O$	White solid	47.5	48.4	12.8	13.3	—
Pb_2EDP	White solid	70 0	69 0	10 4	10.3	—

Thermal analysis of the compounds was done in the atmosphere of air at National Chemical Laboratory, Poona. The specimens were heated at the rate of 10°/min in 20-1000° range and heated alumina was used as standard.

Results and Discussion

Reactions of metal acetates with ethylenediphosphonic acid in aqueous solution yield solid complexes of the general composition $M_2EDP.nH_2O$ where M is Mn(II), Ni(II), Zn(II), Cd(II) or Pb(II) and n = 0, 3 or 4. The structures of these compounds have been elucidated from the infrared, electronic spectral, magnetic measurements and thermogravimetric analytical studies.

The ir spectrum of the free acid shows peaks at 2420 and 1220 cm^{-1} which are characteristic of the P–H and P=O vibrations indicating that the phosphonate form is predominant in the free acid. However, in the ir spectra of metal derivatives phosphoryl frequencies disappear suggesting the formation of metal organophosphite. Formation of the phosphites is indicated from the elemental analysis also. This can be represented as follows :



Similar results have been reported when certain organophosphorus acids containing the P(O)(OH) group were converted to the silver or lead salts[5-7].

Other absorption bands of EDP and its metal derivatives have been given in Table 2.

Table 2—Infrared Spectral Data for Free Ligand and its Different Bivalent Metal Derivatives

Assignments	EDP	Mn(II)	Ni(II)	Zn(II)	Cd(II)	Pb(II)
P=O	1220	—	—	—	—	—
P–H	2420	—	—	—	—	—
(P)–O–C	1090	1090(br)	1080(br)	1090(br)	1050(br)	1040(br)
P–O–(C)	1000	975	980	980	980(sh)	960(sh)

Thermal analysis: The general scheme of thermal decomposition is the same for all complexonates. Only the derivatogram of nickel(II) salt has therefore been given in Fig. 1.

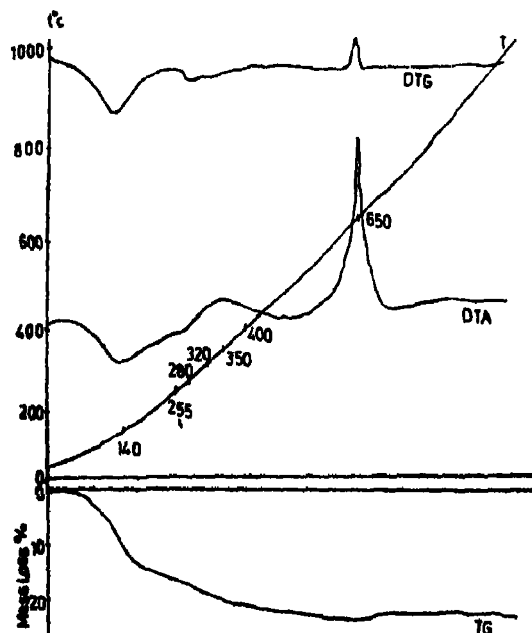


Fig 1. Derivatogram of $Ni_2EDP.4H_2O$ (100 mg specimen).

The thermogravimetric curve for nickel(II) salt shows that it is stable upto 60°. When heated in the temperature range 60-225°, the total loss in mass is 16.5% and it corresponds to loss of 3 moles of water (theoretically reqd. loss = 16.4%). The absence of plateaux or inflections on mass loss curve indicates detachment of strictly determined number of molecules of water. This mass loss is accompanied by a broad endothermic effect with a minima at 140°. In the second stage of decomposition (225-400°) two overlapping effects are observed which can be readily observed in DTG curve. By projection of minima of DTG curve onto the TG curve, the weight losses in two steps are 2.5% (225-320°) and 3.0% respectively. The first one corresponds to the loss of the fourth water molecule (2.6% theoretical) and the second step seems to be the decomposition of organic part. DTA curve shows exothermic peak with a maxima at 350° and has an inflection at 280°. Due to the fast rate of heating perhaps, two clearly separate peaks are not observed. On further heating in the range of 400-600° there is a gradual loss in mass of the specimen amounting to ~2%, showing absence of any stable intermediate. At 650° sharp exothermic peak is observed on DTA curve with slight mass gain.

Calculations show that the final products of thermal decomposition are probably metal oxide and P_2O_5[8]. Theoretical loss is 22.3%, experimental being 22.5%.

Electronic spectra and magnetic moments:

$Ni_2EDP.4H_2O$: The magnetic moment of the title compound at room temperature is 2.24 B. M. For octahedral nickel(II) complexes, magnetic moments lie usually within the range 2.9-3.3 B. M. whereas for tetrahedral nickel(II) complexes the moments ranging from 3.2 to 4.0 B. M. are anticipated depending upon distortion from the ideal T_d symmetry[9]. The anomalous magnetic moment in this case can be attributed to antiferromagnetic interactions.

Electronic spectra, however, permit an unambiguous structural assignment. The diffuse reflectance spectrum of nickel(II) complex shows three bands at 29410; 16670 and 10870 cm^{-1} which arise from the transitions for $^3A_{2g}$ ground state to the excited levels $^3T_{2g}$ (F), $^3T_{1g}$ (F) and $^3T_{1g}$ (P) in the order of increasing energy. ν_1 appears as a doublet which is ascribed to a gain in intensity of $^3A_{2g} \rightarrow {}^1E_g$ transition through configurational interaction with the $^3T_{1g}$ (F) level[10]. The small magnitude of splitting of ν_1 (10630 and 10870 cm^{-1}) is indicative of lowering in symmetry from O_h to C_{2v}[11].

The value of Racah parameter from spin allowed transitions is 898 cm^{-1}, which is 86.3% of free ion value 1041 cm^{-1} and crystal field stabilization energy is 10,870 cm^{-1}.

Mn_2EDP: In the absence of solution spectra it is not possible to assign stereochemistry.

The magnetic moment value at room temperature (3.85 B. M.) lies between those expected for high spin and low spin d^5 octahedral complexes. This is proposed to be due to the presence of thermal equilibrium between spin state $S = \frac{1}{2}$ and $S = 5/2$[9].

$Zn_2EDP.3H_2O$ and $Cd_2EDP.3H_2O$: As expected for d^{10} system, they are dimagnetic in nature.

An attempt to prepare Hg(II) salt resulted in its reduction to mercurous state, which on addition of excess ligand precipitates metallic mercury.

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Tricyclohexyl Tin Halides and Pseudohalides : Structural and Biocidal Activity

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A number of tricyclohexyltin compounds Cy_3SnX where X=Cl^-, Br^-, I^-, NCS^-, NCO^-, NC^-, N_3^-, $NCSe^-$ or CH_3COO^- were obtained from metathetical or neutralization reactions and in case of X=NCO and NCS by fusion of the tin oxide with urea and thiourea respectively The nature of bonding in the pseudohalides has been discussed and some probable structures proposed The antimicrobial activity against a number of pathogenic species have been tested and reported.

CYCLOHEXYLTIN compounds have recently been shown to possess some very interesting properties which place them in a special class. The biocidal activity of tricyclohexyltin compounds was initially reported in the patents[1-3] and the compounds are presently being manufactured commercially. One such compound is the tricyclohexyltinhydroxide $(C_6H_{11})_3SnOH$, trade name 'Plictran'[4]. Some unusual structural features associated with the steric hindrance offered by the cyclohexyl groups are also drawing considerable attention. Thus, the bonding in the tricyclohexyltin acetate and haloacetate permits a unidentate carboxylate linkage giving monomeric products[5,6], whereas all other known triorganotin acetates possess five coordinate tin with a polymeric structure[7]. Furthermore, the absence of amino group coordination to tin in the zwiterionic amino acids of triorganotin compounds[8] and Mössbauer spectral data show that unlike similar compound the simple point charge model does not account for the quadrupole splitting of the cyclohexyltin derivatives[5-9].

In continuation to our studies on various aspects of organotin and lead pseudohalides[10,11], we now report some synthetic and structural studies of tricyclohexyltin compounds, Cy_3SnX, where Cy=Cyclo-C_6H_{11} and X=Cl^-, Br^-, I^-, NCS^-, NCO^-, N_3^-, NC^-, $NCSe^-$, CH_3COO^-, and the *bis* sulfide $(Cy_3Sn)_2S$ along with a comparative study of their biocidal activity against five species of bacteria and six species of fungi.

Materials and Method :

Tricyclohexyltin hydroxide : A Grignard solution was prepared from magnesium (35 g ; 1.43 mole) and cyclohexyl bromide (200 g ; 1.226 mole) in anhydrous ether, in a nitrogen atmosphere. The unreacted magnesium was removed by filtering through glass wool under nitrogen pressure. To the Grignard solution thus obtained, tin tetrachloride (70 g ; 0.26 mole) in dry ether (150 ml) was added dropwise during half an hour. The reaction mixture was stirred for further period of 1 hr followed by addition of benzene and refluxing for 6 hr This gave Cy_4Sn on acid hydrolysis. The reaction of Cy_4Sn with bromine in CCl_4 gave excellent yield of tricyclohexyltin bromide (above 60 %), m. p 76° (lit[12] 77°). The ethanol solution of the bromide on further treatment with aqueous KOH gave Cy_3SnOH. Recrystallized from alcohol ; m. p. 216-18° (lit[12] 220-22°).

Cy_3SnX (X=Cl and I) : The halides, chloride and iodide, were obtained in yields around 75-80 % by the treatment of Cy_3SnOH with the corresponding hydrohalic acid in hot ethanol. The products obtained on concentration were washed twice with cold ethanol to remove the excess of acid and finally recrytallized from petroleum ether (60-80°). Cy_3SnCl, m.p. 128° (lit.[12] 129-30°), Cy_3SnI ; m.p. 65° (lit.[12] 65°).

$Cy_3SnOOCCH_3$. The acetate was prepared by the metathetical reaction between silver acetate and tricyclohexyltin iodide in refluxing benzene or sodium acetate and tricyclohexyltin chloride in absolute ethanol, as needle like crystals (yield 75%). The product was confirmed by mixed m.p. with a sample prepared by literature[12] method viz. heating tricyclohexyltin hydroxide with glacial acetic acid in ethanol.

$Cy_3SnNCSe$: Tricyclohexyltin selenocyanate was prepared by metathetical reaction. Thus, Cy_3SnCl (5 g ; 0.012 mole) in 50 ml of chloroform and KSeCN (2.16 g ; 0.015 mole) in 25 ml of chloroform were mixed and stirred at room temperature for 4 hrs The reaction mixture was filtered off, the filtrate concentrated and the solid so obtained was recrystallized twice from petroleum ether (60-80°) ; yield 60 % ; m.p. 160-62°. Analysis ; Found : C, 48.18 ; H, 6.99 ; N, 2.89 ; Sn, 24.99. Calcd. for $C_{19}H_{33}NSnSe$; C, 48.23 ; H, 7.03 ; N, 2.96 ; Sn, 25.08 %.

Cy_3SnN_3 : A solution of Cy_3SnCl (4 g ; 0.009 mole) in 50 ml ether was mechanically stirred with concentrated aqueous solution of sodium azide in 20 ml of water at room temperature for 2 hr. The ether layer was washed twice with water to remove the excess of sodium azide, the solid obtained after removal of the ether was dried and recrystallized from petroleum ether; m.p. 104° (lit.[24] 104°); yield 70 %.

Cy_3SnNC : Silver cyanide (2.46 g ; 0.018 mole) and tricylohexyltin iodide (3 g ; 0.006 mole) were refluxed for 2 hr in chloroform and stirred at room temperature for overnight. Filtration was followed by washing the residue with chloroform. The filtrate was evaporated to give 68 % tricyclohexyltin cyanide recrystallized from chloroform/benzene mixture; m.p. 280°. Analysis; Found : C, 57.82 ; H, 8.38 ; N, 3.50 ; Sn, 30.08. Calcd. for $C_{19}H_{33}NSn$; C, 57.89 ; H, 8.43 ; N, 3.55 ; Sn, 30.11 %.

Cy_3SnNCO : It was prepared by the metathetical reaction of silver cyanate with tricyclohexyltin iodide in chloroform at room temperature. The precipitated silver iodide was filtered off and the filtrate on concentration yielded tricyclohexyltin isocyanate which was recrystallized from petroleum ether/chloroform mixture ; m.p. 101°.

Tricyclohexyltin isocyanate was also prepared by fusion of Cy_3SnOH and urea in nitrogen atmosphere. Thus, Cy_3SnOH (5 g ; 0.012 mole) and finely powdered urea (0.75 g ; 0.012 mole) was mixed and heated in slow stream of nitrogen. The temperature was gradually raised up to around 200° to bring the mixture into molten form. Subsequently, the temperature was retained between 130-140°. The nitrogen flow removed ammonia and water from the reaction site. The crude reaction product was then cooled and extracted with chloroform to give Cy_3SnNCO, which was recrystallized from petroleum ether/chloroform mixture ; yield 50 % ; m.p. 100°. Analysis ; Found : C, 55.58 ; H, 8.06 ; N, 3.38 ; Sn, 28.88. Calcd. for $C_{19}H_{33}NOSn$; C, 55.63 ; H, 8.10 ; N, 3.41 ; Sn, 28.93 %.

Cy_3SnNCS : It was prepared by metathetical reaction of equimolar ratio of silver thiocyanate and tricyclohexyltin iodide in refluxing chloroform for 2 hr. The precipitated silver iodide was filtered off, the filtrate concentrated and the compound was recrystallized from hexane to give crystals of Cy_3SnNCS ; m.p. 121-22° (lit.[16] 123°).

Cy_3SnNCS was also obtained by heating the tricyclohexyltin hydroxide and thiourea in a nitrogen atmosphere. Thus, equal molar mixture of Cy_3SnOH and thiourea was fused at 180-200° and the temperature was then kept between 130-140° for 4 hr in a slow stream of nitrogen. The intermediate products, ammonia and water, were removed by nitrogen and the crude product was refluxed with chloroform and filtered off. The product was concentrated and kept in ice cold water for 15 min. White needle like crystals formed were separated by filtration and characterized as $(Cy_3Sn)_2S$; yield about 50 %. The filtrate on concentration gave 20 % of Cy_3SnNCS, recrystallized with petroleum ether ; m.p. 120° (lit.[16] 123°) and $(Cy_3Sn)_2S$; m.p. 130-31°.

$(Cy_3Sn)_2S$ obtained in the above reaction was confirmed by mixed melting point of an authentic sample prepared as given below.

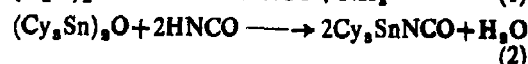
H_2S gas was passed in hot alcoholic solution of Cy_3SnOH, followed by cooling when needle shaped crystals were obtained almost quantitatively which were recrystallized from methanol; m.p. 134°. Analysis ; Found . C, 56.22 ; H, 8.62 ; Sn, 30.82 ; S, 4.12. Calcd. for $C_{36}H_{66}Sn_2S$; C, 56.27, H, 8.65 ; Sn, 30.89 ; S, 4.17 %.

Results and Discussion

Apart from the common methods of metathetical reactions employed for obtaining the tricyclohexyltin derivatives, the isocyanate was also obtained by the fusion of a mixture containing equimolar ratios of Cy_3SnOH or the *bis*-oxide and urea at about 200° for 15 min and then at 130-140° for 4 hr in 50 % yield. A plausible mechanism for the formation of cyanate by fusion with urea is the formation of isocyanic acid (HNCO) at fusion temperature of urea (Eq. 1) followed by its action on the oxide or hydroxide (Eq. 2).



$$(H_2N)_2C{=}O \xrightarrow{\Delta H} HNCO + NH_3 \quad (1)$$



$$(Cy_3Sn)_2O + 2HNCO \longrightarrow 2Cy_3SnNCO + H_2O \quad (2)$$

It is expected that at such temperatures the hydroxide would get dehydrated into the *bis*-oxide.

These reactions are substantiated by the facts that (i) both ammonia and water vapour could be detected escaping through the condenser top, and (ii) preformed isocyanic acid reacts independently with organotin and antimony oxides[16].

Attempts to extend the reaction for obtaining Cy_3SnNCS by using thiourea in place of urea resulted in the formation of only a small percentage of Cy_3SnNCS along with considerable amount of $(Cy_3Sn)_2S$ (cf : experimental) together with escaping ammonia and water. Repeating the experiment in an inert hydrocarbon solvent having boiling point higher than water (e.g., toluene) resulted once again in the formation of the *bis*-sulphide along with some unidentified product. These observations are similar to those obtained by Cummins and Dunn[7] for tributyltin compounds using the fusion method and Raymond *et al*[18] using acetonitrile as solvent for the phenyltin compounds.

The fusion reaction of hydroxide and thiourea resulted in the formation of mostly the *bis*-sulfide and to some extent of the thiocyanate unlike the reaction reported by Raymond *et al*[18] in acetonitrile who reported the formation of dicyanamide

and *bis*-triphenyltin carbodimide. The reaction of tricyclohexyltin compounds and thiourea in toluene or at fusion temperature resulted only in the *bis*-sulfide and the thiocyanate. Some unidentified products obtained in this work could be the cyanamide and carbodimide which could not be separated or identified conclusively. These reactions have been independently and adequately worked up by a number of investigators[14-18] for other triorganotin moieties and are not discussed any further. The cyclohexyl group does not behave differently under these reaction conditions.

Infra-red spectra : All the four pseudohalide groups (viz. NCO, NCS, NCSe and NC) are capable of exhibiting linkage isomerism and have facinated several past workers of group IV organometallic chemistry[19-20]. However, it appears that this is for the first time that an attempt has been made to investigate structurally these anions in combination with a tricyclohexyltin moiety. This is important in view of the anomalous behaviour observed earlier for tricyclohexyltin acetate.

Cy_3SnNCS : A very strong broad band of the asymmetric –NCS stretching with the centre at 2062 cm^{-1} suggests the bonding to be iso(–NCS) i.e., the group is attached through the nitrogen end with the tin metal. Apart from the shape and intensity of the band which has been used to distinguish between the two isomers in the past[21] other important factors in favour of nitrogen linkage are :

(1) The smaller size and greater electronegativity of N permits a stronger d π and p π bond between tin and nitrogen than with diffuse p orbitals of the S atom.

(2) R_3Sn^+(IV) being a hard acid according to HSAB concept would prefer to attach itself to the hard base, that is N rather than S of the thiocyanate[22].

(3) Unlike the organometallics of transition metals, no group(IV) thiocyanate is as yet known to have a S-bonded linkage.

Cy_3SnNCO : In general, oxygen bonded cyanate with metals are rare and the nitrogen bonded products are more common for main group metals. The strong asymmetric –NCO band 2222 cm^{-1} is in the region of reported triorganotin isocyanates. A few inorganic cyanates reported have much lower values for the asymmetric stretch. The bonding –NCO was also observed as a very weak band at around 610 cm^{-1} [19,20].

Cy_3SnNC : The only characteristic band observed for the cyanide is the asymmetric –CN stretching at 2150 cm^{-1} which is closer to organic isonitriles 2160-2120 cm^{-1}, rather than the nitriles 2260-2220 cm^{-1}. However, taking into consideration the heavy mass of the central atom tin and comparatively high m.p. and low solubility, a polymeric carbon bonded cyanide structure is most likely as has been reported earlier from this laboratory[23] for other triorganotin cyanides.

$Cy_3SnSeCN$: The SeCN group like the –SCN gives rise to three fundamental modes of vibration. The iso –NCSe and normal –SeCN forms can be distinguished by the C–Se stretching at 630 ± 20 cm^{-1} for the iso and 530 ± 10 cm^{-1} for the normal forms[24]. The tricyclohexyltin (iso) selenocyanate show a broad band of 605 cm^{-1} which suggests Sn-NCSe bonding. The theoretical reasons advanced earlier for the bonding in the thiocyanate derivatives are equally valid for the selenocyanate as well, and add further support to tin-nitrogen bonding in the molecule. Once again all the organometal selenocyanates, Tl[24], Te[26], Ge, Sn[19] Pb[25], reported so far possess an –iso bonding.

Cy_3SnN_3 : The azide group in tricyclohexyltin azide, though not capable of showing structural isomerism, provides enough evidences in favour of a covalently bonded group. This is evident from its high solubility in organic solvents, smooth and sharp melting point and the asymmetric stretching at 2065 cm^{-1} followed by bands at 1280 cm^{-1} and 670 cm^{-1} which agree well with earlier reports regarding the covalent bonded triorganotin azides from this laboratory[27].

TABLE 1—INFRARED ABSORPTION OF THE PSEUDOHALIDES. WAVE LENGTH IN cm^{-1}

Compound	asym	sym	δ
$(C_6H_{11})_3SnNCO$	2222 vs	1350 m	615 w
$(C_6H_{11})_3SnNC$	2150 vs	—	—
$(C_6H_{11})_3SnNCS$	2062 vs	1040 m	670 ± 5 m
$(C_6H_{11})_3SnNCSe$	2050 vs	605 m	480 m
$(C_6H_{11})_3SnN_3$	2065 vs	1285 m	670 m

asym = asymmetric, sym = symmetric, vs = very strong, m = medium, w = weak.

The adsorption associated with the tricyclohexyltin moiety agree well with those reported earlier in combination with the anion (OH^- and CO_3^{--})[28] and hence are not listed or discussed.

The preferred equilibrium solid state molecular structure for tin in most triorganotin compounds containing uninegative anions R_3SnX is polymeric trigonal bipyramid, where the three organic groups are arranged on the planar ring and the anion X acts as bridging group above and below the plane of the ring[7]. The angular distortions from perfect geometry are generally in the directions dictated by the isovalent hybridization or VSEPR theories. The role of steric bulk of the organic group or the anion is crucial in deciding the structure and no authenticated hexacoordinated R_3Sn derivative is yet known. In the tricyclohexyltin compounds reported in this work, the ir bands, the high m.p. all above 100 with exception where X=Br (m.p 77°) and I (m.p. 65°) are, in favour of an associated trigonal bipyramidal structure. These physical data compare very favourably with the corresponding phenyl, methyl and butyl compounds, all of which have associated structures. Further support of the tricyclohexyltin compounds can only be had through single crystal analysis. The exception of bromine

TABLE 2—ANTIMICROBIAL ACTIVITY OF TRICYCLOHEXYLTIN COMPOUNDS

Compound	Antibacterial activity (μg/ml)*					Antifungal activity (μg/ml)*					
	S.a	*S.t.*	*E.c.*	*K.p.*	*S.f.*	*C.n*	*T.m.*	*A.n*	*A.f.*	*M.c.*	*C.a.*
Cy_3SnNCS	0.78	>100	>100	1.75	1.56	0.78	12.5	25.5	12.5	12.5	1.56
Cy_3SnNCO	0.78	>100	>100	1.75	1.56	0.78	12.5	25.5	12.5	12.5	1.56
Cy_3SnNC	0.78	>100	>100	1.75	1.56	0.78	25	25.5	12.5	25.5	1.56
$Cy_3SnNCSe$	0.78	>100	>100	1.75	1.56	0.78	6.25	25.5	12.5	12.5	1.56
Cy_3SnN_3	3.25	>100	>100	1.75	12.5	0.78	12.5	25.5	12.5	12.5	1.56
Cy_3SnOH	1.56	>100	>100	3.12	6.25	1.56	6.25	1.56	6.25	3.25	6.25
Cy_3SnCl	3.25	>100	>100	6.25	12.5	3.125	6.25	0.78	6.25	3.125	12.5
Cy_3SnBr	3.25	>100	>100	3.12	12.5	3.125	6.25	0.78	12.5	3.125	12.5
Cy_3SnI	6.25	>100	>100	6.25	12.5	12.5	6.25	0.78	12.5	2.125	12.5
$Cy_3SnOOCCH_3$	3.25	>100	>100	3.12	6.25	1.56	1.56	3.25	12.5	1.56	6.25

Cy=CyClO $-C_6H_{11}$. *All these compounds were tested *in vitro* for antibacterial activity against *S a* = *S aureus*, *S.t.* = *S. typhi*, *E.c.* = *E. coli*, *K.p.* = *K pneumoniae*, *S.f* = *S. faecalis*, and antifungal activity against *C.n.* = *neoformans*, *T.m.* = *T. mentagrophytes*, *A.n* = *A. niger*, *A f* = *A fumigatus*, *M c.* = *M. canis*, *C a* = *C albicans*. The minimum inhibitory concentration was expressed in terms of microgram per millilitre (μg/ml) at which the growth of test organism was completely inhibited.

ınd iodine may be due to both the bulkier and veak coordinating nature of these anions which nay favour four coordination and a monomeric structure to these compounds. The steric effect of he pseudohalides of this investigation is considerably reduced when we consider that the N bonded isomers have a linear arrangement of the hree atoms -N=C=X as compared to the bent chalcogen (O, S, Se) isomer[24]. It may be added hat the only examples of the completely characterized four coordinated triorganotin system, tricyclohexyltin acetate and trifluoro acetate[6], have infrared frequencies very different from other polymeric triorganotin acetates These molecules adopt a flattened tetrahedral structure with wide carbon angle at tin as expected from both electron redistribution in the frame work and steric repulsion of bulky cyclohexane ring. The quadrupole splittings of the fluoride and chloride are similar to hose reported for the methyltin analogues indicating five coordinate structure. In contrast, the bromide and iodide give quadrupole splittings which are midway between those found for polymeric trimethyltin and monomeric trineophenyltin bromide and iodide indicating a very weak intermolecular association if at all[22].

In view of the above facts the bromide and he iodide offer a good example which requires single crystal X-ray analyses to confirm the above predictions.

Biological activity: The antimicrobial activity of tricyclohexyltin halides and pseudohalides was examined *in vitro* aginst six species of fungi, *C. albicans*, *C. neoformans*, *M. canis*, *A. niger*, *A. Fumigatus*, *T. mentagrophites*, and five species of bacteria, *S. aureus*, *S. typhi*, *E. Coli*, *S. faecalis*, *K. pneumoniae*. The compounds exhibited higher activity *in vitro*.

It has been reported that triorganotin R_3SnX compounds where $R{=}nBu$, $Cy{-}C_6H_{11}$, Ph and neophenyl are widely used in industry as biocides. Their biological activity is due mostly to the organotin part of the molecule[20]. It can be seen that the high antimicrobial activity of tricyclohexyltin compounds compare favourably with that of phenyl tin compounds and some cases possess even higher activity.

The antimicrobial activity of ethanolic solution of the compounds has been ascertained by twofold serial dilution method-Sabourauds and neutrient broths were used as test media for fungi and bacteria respectively. The maximum concentration of the compounds tested was 100μg/ml. The bacteria used were *S. aureus*, resistent in 2500 units penicillin/ml. The fungi were incubated at 25±1° and the bacteria at 37°; incubation period for both was 24 hr. The antibacterial and antifungal activities are listed in Table 2.

An excellent activity is observed against penicillin resistant gram-positive *S. aureus*, while the gram negative species *S. typhi* and *E. coli* appears better to extremely resistant, to all tricyclohexyltin halides. Organotin pseudohalide compounds were found most active against the fungi *C. neoformans*. Once again, better than the halide in particular, they have been shown to inhibit only gram positive bacteria. The large activity of tricyclohexyltin halides and pseudohalides may be attributed to the presence of cyclohexyl moiety and a pseudohalide group.

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Preparative and Structural Studies on Bimetallic Tetradithiocarbamates of Some Bivalent 3d-Metal Ions

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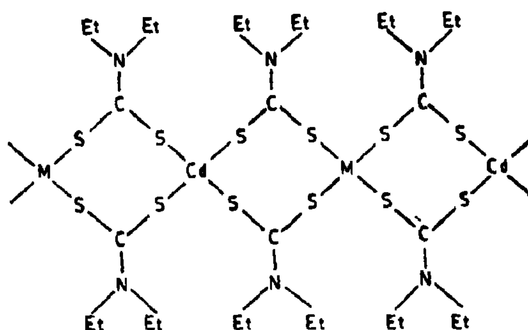
Some novel bimetallic tetradithiocarbamates, $MCd(Dtc)_4$, M=VO(IV), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); Dtc=piperidine dithiocarbamate (pDtc) or diethyldithiocarbamate (Et_2Dtc), have been prepared for the first time and characterised on the basis of analytical data, molar conductance, magnetic susceptibility, electronic, esr and infrared spectral measurements. Tetrahedral coordination around Zn(II) and Cd(II), square pyramidal coordination arouud VO(IV) and square planar coordination around Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been proposed in bimetallic tetradithiocarbamates

ALTHOUGH an extensive literature[1-9] is available on synthesis and structural characterisation of transition metal(II) dithiocarbamates, there is no previous work on bimetallic tetradithiocarbamates. A preparative and structural study of $MM'(Dtc)_4$ [M'=Zn(II), Cd(II) or Hg(II); M=VO(IV), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); Dtc= dimethyl, diethyl, dibutyl, disopropyl, piperidinyl dithiocarbamate] and their complexes with Lewis bases containing one or more donor atoms such as nitrogen, oxygen, sulphur and phosphorus was undertaken and the present paper describes the results of our investigations on $MCd(Dtc)_4$ complex, M=VO(IV), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II); Dtc=piperidine dithiocarbamate, diethyldithiocarbamate.

Experimental

All chemicals used were B.D.H.(LR) grade. Sodium salts of piperidine dithiocarbamate and diethyldithiocarbamate were prepared by the known method[9,10] (Found : C, 32.51 ; H, 4.69 ; N, 6.21 ; S, 29.20. Calcd. for $C_6H_{10}NS_2Na.2H_2O$; C, 32.86 ; H, 4.59 ; N, 6.38 ; S, 29.24 % and Found : C, 25.47 ; H, 7.45 ; N, 6.71 ; S, 28.17. Calcd. for $C_5H_{10}NS_2Na.3H_2O$; C, 26.66 ; H, 7.15 ; N, 6.21 ; S, 28.46 %).

Synthesis of complexes : $Na_2[Cd(pDtc)_4]$ and $Na_2[Cd(Et_2Dtc)_4]$ were prepred *in situ* by gradual addition of $Cd(NO_3)_2$ solution in acetone-water (80 : 20, v/v) to a solution of NapDtc or $NaEt_2Dtc$ in the same solvent mixture in 1 : 4 molar ratio with vigorous stirring. The complexes $MCd(Dtc)_4$ were prepared by gradual addition with constant stirring of a solution of metal nitrate to a solution of $Na_2[Cd(pDtc)_4]$ or $Na_2[Cd(Et_2Dtc)_4]$ prepared *in situ* as described above in 1 : 1 molar ratio in acetone-water (80 : 20, v/v). The complexes thus precipitatated were filtered immediately to avoid the formation of $Cd(Dtc)_2$ and washed with the above solvent mixture and then with ether and dried in vacuum.

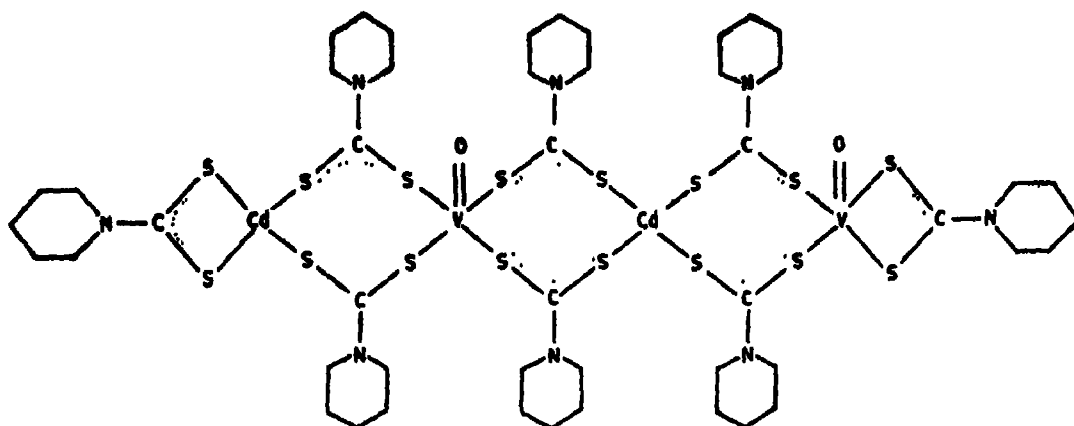


$MCd(Et_2Dtc)_4$, M=VO(IV), Mn(II), Fe(II), Co(II), Ni(II), Cu(II)

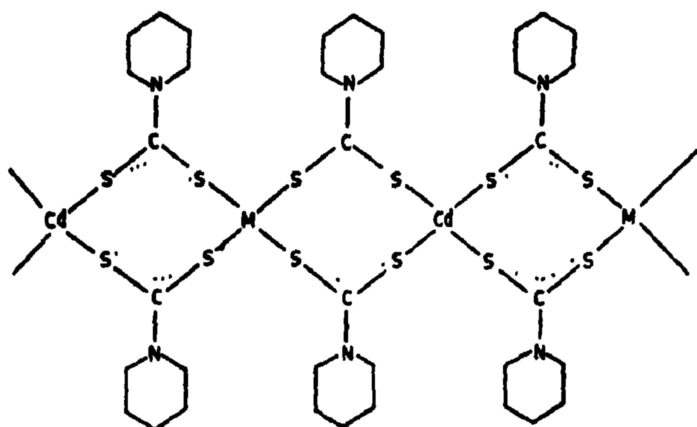
Analysis of the complexes : The complexes were analysed for metals using standard literature procedures[11]. Sulphur was estimated as $BaSO_4$ and nitrogen microanalytically. The analytical data are given Table 1.

Physical measurements : Molar conductance of the complexes in nitrobenzene at $10^{-3}M$ concentration was measured with WTW conductivity meter. Magnetic susceptibility measurements were made at room temperature on Cahn-Faraday electro balance using $HgCo(NCS)_4$ as calibrant and experimental magnetic susceptibilities were corrected for diamagnetism. Molar conductance and magnetic moment data are included in Table 1. Electronic spectra of NapDtc and $NaEt_2Dtc$ and complexes were recorded on Cary—14 spectrophotometer in nujol while the ir spectra were recorded on a Perkin Elmer spectrophotometer model-621 in nujol (4000-200 cm^{-1}) and in KBr (4000-400 cm^{-1}). The absorption bands of diagnostic value and their assignments are given in Table 1. ESR spectra were recorded as chloroform solution both at room and liquid nitrogen temperatures on a Varian X-band spectrometer model E-4 using DPPH as an

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$VOCd(pDtc)_4$



$MCd(pDtc)_4$, M = Mn(II), Co(II), Ni(II), Cu(II) or Zn(II)

TABLE 1—ANALYTICAL DATA, COLOUR, MOLAR CONDUCTANCE, MAGNETIC MOMENTS AND DECOMPOSITION TEMPERATURE OF THE COMPLEXES

Complex	Colour	Found (Calcd.)(%) M	Cd	N	S	Molar conductance ($\Omega^{-1}cm^2mole^{-1}$)	μ_{eff} (B.M.)	Decomposition Temperature (°C)
$VOCd(pDtc)_4$	Dirty yellow	6.15 (6.20)	14.00 (18.72)	6.70 (6.82)	30.53 (31.26)	0.59	1.74	197*
$VOCd(Et_2Dtc)_4$	Dirty yellow	6.31 (6.59)	14.12 (14.55)	7.00 (7.37)	32.92 (33.22)	0 58	1.69	132
$MnCd(pDtc)_4$	Violet	6.89 (6.79)	18.64 (18.90)	7.17 (6.92)	31.62 (31.66)	0.21	3.85	165
$MnCd(Et_2Dtc)_4$	Violet	8.82 (9.09)	15.21 (14.78)	7.00 (7.37)	32.50 (38.76)	0.22	4.40	102
$FeCd(Et_2Dtc)_4$	Dark brown	6.89 (7.38)	15.28 (14.77)	7.01 (7.36)	32.71 (33.70)	0.31	3.30	178
$CoCd(pDtc)_4$	Green	7.10 (7.25)	18.60 (18.83)	6.70 (6.89)	31.10 (31.57)	0.30	2.37	280
$CoCd(Et_2Dtc)_4$	Green	7.39 (7.71)	14.20 (14.71)	6 89 (7.38)	32.78 (33.57)	0.61	2.52	219
$NiCd(pDtc)_4$	Olive green	6.70 (7.22)	18.05 (18.83)	6.58 (6.89)	30.90 (31.58)	0.07	diamag.	248
$NiCd(Et_2Dtc)_4$	Olive green	7.11 (7.68)	18.69 (14.71)	7.20 (7.38)	32.77 (33.58)	0.11	diamag.	204
$CuCd(pDtc)_4$	Chocolate	7.55 (7.77)	18.60 (18.75)	6.58 (6.85)	31.45 (31.89)	0.12	1.78	228
$CuCd(Et_2Dtc)_4$	Chocolate	8.17 (8.25)	14.01 (14.60)	7.31 (7.27)	32.75 (33.32)	0.15	1.70	155
$ZnCd(pDtc)_4$	White	7.65 (6.98)	13.80 (18.72)	6.90 (6.84)	31.10 (31.32)	0.07	diamag.	286

* Melting point.

internal reference. The in-plane σ-bonding parameter (α^2) was calculated according to the method[18] of Narayana and Sastry.

Results and Discussion

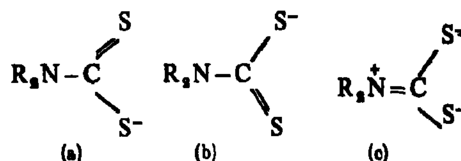
The analytical data indicate the formation of complexes of general formula $MCd(Dtc)_4$. All the complexes decompose in 102-280° temperature range except $VOCd(pDtc)_4$ which melts at 197°. The complexes are insoluble in water and common organic solvents but slightly soluble in nitrobenzene and chloroform. Due to insolubility of the complexes we could neither grow single crystal of the complexes nor determine their molecular weights. Our structural studies were therefore, confined to molar conductance, magnetic susceptibility, electronic, esr and ir spectral measurements. The very low molar conductance values indicate the non-electrolytic[13] nature of the bimetallic tetradithiocarbamates.

Magnetic susceptibility measurements : The magnetic moments of oxovanadium(IV) and Cu(II) complexes indicate the presence of one unpaired electron. The μ_{eff} values of Mn(II) complexes are consistent with quartet[14](S=3/2) ground state and eliminate the possibility of any dominant antiferromagnetic type of exchange interaction. The magnetic moments of Fe(II) complex is indicative of low-spin nature of the complex. While Ni(II) complexes are diamagnetic, cobalt(II) complexes have magnetic moments of 2.37 B.M. for $CoCd(pDtc)_4$ and 2.52 B.M. for $CoCd(Et_2Dtc)_4$ showing square planar geometry around Ni^{2+} and Co^{2+} ions[15].

Electronic spectral studies : $VOCd(pDtc)_4$ and $VOCd(Et_2Dtc)_4$ exhibit three bands at 11765, 16000, 22220 cm^{-1} and at 11110, 17390 and 23530 cm^{-1} assigned to $d_{xy}\rightarrow d_{yz}$, d_{xz}, $d_{x^2-y^2}$ transitions respectively assuming square pyramidal geometry[16] with C_{4v} symmetry. Two bands observed at 10255 cm^{-1} and 15870 cm^{-1} for $CoCd(pDtc)_4$ and at 10255 cm^{-1} and 15700 cm^{-1} for $CoCd(Et_2Dtc)_4$ are attributed to $d_{x^2-y^2}\rightarrow d_{yz}$ and $d_{yz}\rightarrow d_{zy}$ transitions in square planar geometry respectively. The band at 10255 cm^{-1} being the most characteristic of square planar[17] geometry may be taken as equal to 15 B from which B works out to 683.7 cm^{-1} for both the complexes. The two d-d transition bands at 16000 cm^{-1} and 21051 cm^{-1} in $NiCd(pDtc)_4$ and $NiCd(Et_2Dtc)_4$ are assigned to d_{xz}, $d_{yz}\rightarrow d_{x^2-y^2}$ and $d_{xy}\rightarrow d_{x^2-y^2}$ transitions respectively assuming square planar geometry[18] with D_{4h} symmetry around Ni(II). The orbital parameter[19] Δ_1 was calculated from the first spin-allowed d-d transition band by assuming a correction factor[20,21] ($F_2=10F_4=800$ cm^{-1}) of 2800 cm^{-1} for Ni^{2+}. The Δ_1 values are the same for both the complexes and place the pDtc and Et_2Dtc in the spectrochemical series of sulphur donors[22] as follows : maleonitriledithiolate (14490) < diethyldithiophosphate (17300) < dithioacetylacetone (17690) ≃ 1-phenyl-5-methyl-2, 4-dithiobiuret anion (17710) < dithiomalonamide anion (17950) < ethylxanthate (18300) < dithiobiuret anion (18430) < diethyldithiocarbamate (18600) ≃ piperidine dithiocarbamate (18,800) < 2,3-dimercaptopropanol anion (19000) < dithiomalonate (20200) < dithiooxalate (20500). A broad band observed at 22725 cm^{-1} in visible spectrum of $CuCd(pDtc)_4$ and two bands at 14815 cm^{-1} and 22272 cm^{-1} in $CuCd(Et_2Dtc)_4$ are attributed to d-d transition in square planar geometry[23].

ESR spectral studies : The room temperature esr spectrum of $CuCd(Et_2Dtc)_4$ complex in chloroform solution consists of a quartet ($g_{iso}=2.0504$ and $A_{iso}=77.5$ G). While the frozen solution spectrum is consistent with a $(d_{z^2})^1$ ground state[24] in as much as it shows the well resolved parallel features, the g-values being in the order : $g_\perp(2.0734) > g_\parallel(2.0044) \approx g_e(2.0023)$. This rules out the possibility of the presence of $Cu(Et_2Dtc)_2$ in our complex as an amorphous mixture with $Cd(Et_2Dtc)_2$, since $Cu(Et_2Dtc)_2$ has $(d_{x^2-y^2})^1$ ground state as evidenced by its frozen solution[25] as well as Zn and Ni diluted single crystal[26] esr spectral studies. The in-plane σ-bonding parameter α^2 is found to be 0.717 indicating a considerable covalency in the Cu – S bond. The reversal of ground state in our $CuCd(Et_2Dtc)_4$ is probably due to bridging bidentate behaviour of Dtc ion as compared to its chelating bidentate behaviour in $Cu(Et_2Dtc)_2$. The greater affinity of sulphur for Cd^{2+} as compared to Cu^{2+} causes the weakening of Cu – S bond which is further supported by the increase in α^2 (0.717) value compared to its value 0.5929 in $Cu(Et_2Dtc)_2$ complex.

Infrared spectra : Dithiocarbamate ion may exist in three possible resonating forms :



It has been shown from ir spectral studies that the main contributing structure is (c) in metal dithiocarbamates. This conclusion is based[27-29] on the fact that $\nu(C=\overset{+}{N})$ (thioureide band) observed in 1480-1550 cm^{-1} region occurs in between the regions for ν(C – N) (1250-1350 cm^{-1}) and ν(C = N) (1640-1690 cm^{-1}). The band observed at 1420-1440 cm^{-1} in ir spectra of Dtc complexes is accordingly assigned[30,31] to $\nu(C=\overset{+}{N})$. The C=S stretching frequency[32-34] has been used to distinguish between the uni- and bidentate nature of dithiocarbamate group. If Dtc is bidentate, as in $Zn(S_2CNEt_2)_2$, a single band at 995 cm^{-1} is observed, whereas a doublet (at 1005, 983 cm^{-1}) is obtained for unidentate Dtc as in EtS_2CNEt_2. The occurrence of a single ν(C ⩦ S) band in 990-1000 cm^{-1} region in all our Dtc complexes, therefore, shows the uninegative bidentate behaviour of Dtc. A strong

band at 970 cm^{-1} is attributed to ν(V=O) in vanadyl complex. The non-ligand bands occuring at 345-380 cm^{-1} and 385-420 cm^{-1} are tentatively assigned to ν(M–S)[34] and ν(Cd–S)[35] modes respectively. Based on analytical data and physico-chemical studies, polymeric structure is proposed for bimetallic tetrabisdithiocarbamato complexes.

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Some New β-Diketonates of Boron : Their Syntheses and Characterisation

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A number of substituted β-diketonates of boron having general formula $\overline{OGOBOC(R)\overline{C:CON(R')N:CCH_3}}$ (where G = C_6H_4, $C_6H_4CH_2$ and $-CH_2C(CH_3)_2CH_2$; R = CH_3, C_2H_5, C_6H_4Cl ; R' = C_6H_5) have been synthesised by the reactions of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones (acyl = acetyl, propionyl, benzoyl and chloro-benzoyl) with 2-isopropoxy 4H-1, 3,2-benzodioxaborin, 2-isopropoxy 1,3,2-benzodioxaborole and 2-isopropoxy 5,5-dimethyl 1,1,3,2-dioxaborinane.

These derivatives have been characterised by elemental analyses and molecular weight determinations The tetra coordination around boron atom in these complexes have been proposed on the basis of ir and pmr spectral evidences.

A survey of literature reveals that 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones (AcMPPOH) behave like β-diketones even in the presence of a heterocyclic ring system and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPPOH) has been widely used in solvent extraction of various transition[1-3] and rare earth metals[4-6].

The present communication deals with the synthesis and characterisation of a number of boron complexes with the above class of ligands. Attempts have been made to establish their probable structure on the basis of ir and pmr spectral evidences

Experimental

All manipulations were carried out under anhydrous conditions. Alkoxy/aryloxy boranes were prepared by literature[7] method. The ligands were synthesised by the method reported by Jensen[8] and were crystallised from *n*-heptane before use. Their purity was confirmed by m.p., tlc and spectral evidences. All the solvents were dried before use.

Synthesis of boron β-diketonates : The reactions of alkoxy/aryloxy boranes were carried out with 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones in 1 : 1 molar ratio in refluxing benzene. Few representative reactions were also carried out in diethyl ether at room temperature. Since a similar pattern was followed in the synthesis of all the derivatives, the synthesis of only one derivative in both the media has been given in detail and the rests have been summarised in Table 1.

Reaction of 2-isopropoxy 1,3,2-benzodioxaborole with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one in 1 : 1 molar ratio in benzene : A benzene solution of 4-bezoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (2.47 g ; 1 mole) was mixed with the benzene solution of 2-isopropoxy 1,3,2-benzodioxaborole (1.58 g ; 1 mole). The solution was refluxed over fractionating column. The isopropanol liberated during the course of the reaction was removed azeotropically with benzene. The progress of the reaction was followed by estimating the isopropanol in the azeotrope. After completion of the reaction, the excess solvent was distilled off and the compound was dried under reduced pressure. The compound was recrystallised from *n*-hexane-benzene mixture, yield 3.34 g (Calcd. 3.42 g) ; m.p. 267°. Found B, 2.72 ; C, 69.47, H, 4.32. Calcd. B, 2.85 ; C, 69.69 ; H, 4.29 %

Reaction of 2-isopropoxy 1,3,2-benzodioxaborole with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one in 1 : 1 molar ratio in ether : Interaction between 2-isopropoxy 1,3,2-benzodioxaborole (0.79 g ; 1 mole) and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (1.24 g ; 1 mole) resulted in simultaneous precipitation of a yellow product. The solid product was filtered, washed with ether and was dried under reduced pressure to yield a yellow coloured boron compound 1.61 g (Calcd. 1.76 g) having similar analysis as mentioned above.

Analytical methods and physical measurements : Boron was estimated as methyl borate[9] and isopropanol was estimated by oxidation with N $K_2Cr_2O_7$ in 12.5 % H_2SO_4[10]. IR spectra were recorded as nujol mull by a 577-Perkin Elmer double grating spectrophotometer. PMR spectra were recorded in $CDCl_3$ using TMS as internal standard by a Varian S-100 spectrophotometer. Carbon, hydrogen were analysed by Coleman-33 carbon hydrogen analyser. Molecular weights were determined ebullioscopically with Gallenkamp ebulliometer equipped with thermister sensor.

Results and Discussion

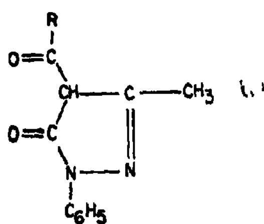
4-Acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones

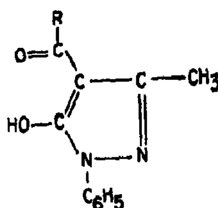
TABLE 1—PHYSICAL AND ANALYTICAL DATA FOR SUBSTITUTED BORON β-DIKETONATES

Sl. No.	Complexes*	Physical state	m.p.† °C	%B Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)	Molecular weight Found (Calcd.)
1.	$OC_6H_4OBO_2N_2C_{12}H_{11}$	Yellow powder	176	3.20 (3.24)	64.90 (64.66)	4.58 (4.49)	342 (334)
2.	$OC_6H_4OBO_2N_2C_{13}H_{13}$	Pink powder	194	3.08 (3.10)	65.38 (65.51)	4.78 (4.86)	352 (348)
3.	$OC_6H_4OBO_2N_2C_{17}H_{13}$	Yellow powder	267	2.91 (2.85)	69.47 (69.69)	4.32 (4.29)	402 (396)
4.	$OC_6H_4OBO_2N_2C_{17}H_{12}Cl$	Light brown powder	202	2.58 (2.50)	—	—	—
5.	$OC_6H_4CH_2OBO_2N_2C_{12}H_{11}$	Orange red powder	146	3.02 (3.10)	65.81 (65.51)	4.80 (4.88)	361 (348)
6.	$OC_6H_4CH_2OBO_2N_2C_{13}H_{13}$	Light yellow powder	106	3.06 (3.10)	—	—	—
7.	$OC_6H_4CH_2OBO_2N_2C_{17}H_{13}$	Yellow powder	164	2.66 (2.68)	70.44 (70.24)	4.38 (4.63)	420 (410)
8.	$OC_6H_4CH_2OBO_2N_2C_{17}H_{12}Cl$	Yellow powder	181	2.88 (2.42)	—	—	—
9.	$OCH_2C(CH_3)_2CH_2OBO_2N_2C_{12}H_{11}$	Brown viscous liquid	—	3.21 (3.29)	—	—	—
10.	$OCH_2C(CH_3)_2CH_2OBO_2N_2C_{13}H_{13}$	Brown viscous liquid	—	3.04 (3.14)	—	—	—
11.	$OCH_2C(CH_3)_2CH_2OBO_2N_2C_{17}H_{13}$	Yellow solid	90	2.60 (2.66)	—	—	—
12.	$OCH_2C(CH_3)_2CH_2OBO_2N_2C_{17}H_{12}Cl$	Yellow powder	110	2.48 (2.54)	62.08 (62.19)	5.04 (5.18)	442 (424.5)

* $C_{12}H_{12}N_2O_2$ = 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one.
$C_{13}H_{14}N_2O_2$ = 4-propionyl-3-methyl-1-phenyl-2-pyrazolin-5-one
$C_{17}H_{14}N_2O_2$ = 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one.
$C_{17}H_{13}N_2O_2Cl$ = 4-chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one.
† All melting points are uncorrected and in the range of ±1°.

(AcMPPOH) are known to exist in both keto and enol forms.

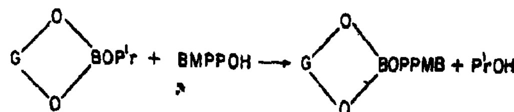

Keto Form


Enol Form

The existence of either of the two forms depends solely upon the nature of the solvents used for crystallisation[8]. The enolic form only interacts with alkoxy/aryloxy borane. Hence, all the ligands have been repeatedly crystallised from *n*-heptane solution to obtain the pure enolic form.

Since the reactions of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones with isopropyl borate were found to be very slow, mono-isopropoxy glycolate derivatives of boron were used for the synthesis of boron β-diketonates.

The reactions of $\overline{OGO}BOPr^i$ [where G = C_6H_4, $C_6H_4CH_2$ and $CH_2C(CH_3)_2CH_2$] were carried out with 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one [BMPPOH] in 1 : 1 molar ratio at room temperature in ether solution.



In the case where G = C_6H_4, the reaction product separated out instantaneously on addition

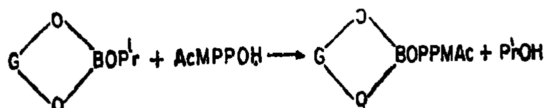
TABLE 2—PMR SPECTRA DATA FOR SUBSTITUTED β-DIKETONES AND THEIR BORON DERIVATIVES IN δ WITH REFERENCE TO TMS

Sl. No.	Compound	Ring CH_3 (ligand)	Phenyl protons (ligand)	Phenyl proton (Boron glycolate)	CH_3 (C_2H_5 or CH_3 of ligand)	CH_2 (C_2H_5 of ligand)	CH_2O (Boron glycolate)
1.	$C_{12}H_{12}N_2O_2$	2.40s	7.2-8.0m	—	2.60s	—	—
2.	$C_{13}H_{14}N_2O_2$	2.44s	7.2-8 0m	—	1.15-1.3t	2.6-2.9q	—
3.	$C_{17}H_{14}N_2O_2$	2.0s	7.1-7.9m	—	—	—	—
4.	$C_{17}H_{13}N_2O_2Cl$	1.95s	7.1-7.9m	—	—	—	—
5.	$OC_6H_4OBO_2N_2C_{12}H_{11}$	2.48s	7.21-7.86m	6 81s	2.58s	—	—
6.	$O_6H_4OBO_2N_2C_{13}H_{13}$	2.43s	7.21-7.86m	6.80s	1.2-1 60t	2.7-2.95q	—
7.	$OC_6H_4OBO_2N_2C_{17}H_{13}$	2.24s	7.21-7.86m	6.82s	—	—	—
8.	$OC_6H_4CH_2OBO_2N_2C_{13}H_{13}$	2.10s	7.0-7.86m	6.7-7.0m	1.2-1.4t	2.7-2 95q	4.86s
9.	$OC_6H_4CH_2OBO_2N_2C_{17}H_{13}$	2.20s	7.21-7.81m	6.81-7.0m	—	—	5.0s
10.	$OC_6H_4CH_2OBO_2N_2C_{17}H_{12}Cl$	2.10s	7.19-7.80m	6.70-7.8m	—	—	5 0s
11.	$OCH_2C(CH_3)_2CH_2OBO_2N_2C_{17}H_{13}^*$	2.20s	7.21-7.80m	—	—	—	3.70s

* gem $C(CH_3)_2$ was observed at δ 0.90.
s=singlet, m=medium, t=triplet, q=quartet.

of the reactants whereas in the similar reaction where $G=C_6H_4CH_2$, the resulting product could be obtained only after about 8 hr of stirring. In the reaction where $G=CH_2C(CH_3)_2CH_2$, no product was isolated even after prolonged stirring at room temperature.

The reactions of $OGOBOPr^i$ [where $G=C_6H_4$ and $C_6H_4CH_2$ and $CH_2C(CH_3)_2CH_2$] were also carried out with 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one in benzene solution. The isopropanol liberated in the reaction was fractionated off azeotropically with benzene and the progress of reaction was evaluated by estimating the amount of isopropanol in the azeotrope at different intervals.



The reactions where $G=C_6H_4$ and $C_6H_4CH_2$ were found to be quite facile, whereas the reactions where $G=CH_2C(CH_3)_2CH_2$ were found to be sluggish and could only be completed after a prolonged refluxing (~30 hr).

Attempt has also been made to study the reaction of 2-isopropoxy 4,4,6-trimethyl 1,1,3,2-dioxaborinone with BMPPOH in refluxing benzene. Although a small amount of isopropanol was detected in the azeotrope in about 30 hr of refluxing, the corresponding derivative could not be obtained.

These observations led us to conclude that $OC_6H_4OBOPr^i$ (A) is more reactive as compared to $OC_6H_4CH_2BOPr^i$ (B) and $OCH_2C(CH_3)_2CH_2OBOPr^i$ (C). (A) is expected to exhibit a higher Lewis acidic character as compared to that of (C) because of the electron sink nature of catachol moiety in (A) which enhances its reactivity towards AcMPPOH. The presence of CH_2 group reduces the electron sink nature of catacholate moiety to some extent and hence B is comparatively less reactive than (A).

All these derivatives have been obtained as coloured solids or viscous liquids, non-volatile in nature. They are soluble in benzene and chloroform but are insoluble or sparingly soluble in carbon tetrachloride and other common organic solvents. These derivatives are found to be monomeric in refluxing benzene.

Infrared spectra : A new medium intensity band appears at 710-730 cm^{-1} in the ir spectra of all boron complexes and can be assigned to B←O[11]. Another important stretching vibration observed at 1515-1490 cm^{-1} in boron chelates has been assigned to $\nu C=O$ stretching frequency which appears in the spectra of ligands at 1540 ± 5 cm^{-1}. This shifting of 30-40 cm^{-1} suggests that the coordination is through carbonyl oxygen. Some new bands appearing in the range of 1340-1260 cm^{-1} have tentatively been assigned $\nu B-O$[12]. All other bands observed in the ligands spectra remained unaffected even after complexation.

PMR spectra : The pmr signals of the ligands and their boron complexes are given in Table 2. The pmr spectra of the ligands show a sharp singlet

TABLE 1—PHYSICAL CONSTANTS AND ELEMENTAL ANALYSIS OF 2-AMINO-5-ARYL-1,3,4-OXADIAZOLES

Product	X	m.p. (°C)	Yield (%)	Elemental analysis : Found (Calcd.)(%) C	H	N
IIa	H	242[A]	85	59.08 (59.63)	4.30 (4.35)	26.00 (26.09)
IIb	4-OCH_3	246[B]	80	56.91 (56.54)	4.65 (4.71)	21.68 (21.99)
IIc	4-Cl	274	87	48.46 (49.10)	3.01 (3.07)	21.32 (21.48)
IId	4-NO_2	250	80	45.91 (46 60)	2.86 (2.91)	27.03 (27.18)
IIe	2,4,5-$(OCH_3)_3$	255	75	52 07 (52 59)	5.15 (5.18)	16.61 (16.73)
IIf	3,4,5-$(OCH_3)_3$	270	78	52.11 (52 59)	5.13 (5.18)	16.63 (16.73)
IIg	3-NO_2	262	82	46.09 (46.60)	2.85 (2.91)	27.06 (27.18)
IIh	4-$N(CH_3)_2$	258	74	58 38 (58.82)	5.83 (5.88)	27.34 (27.45)

A, lit.[6] m.p. 241-243°, B, lit.[6] m.p. 248-249°

TABLE 2—IMPORTANT IONS OBSERVED IN THE MASS SPECTRA OF THE COMPOUNDS *2a-e*

Compound	Ion *1* (M^+) (m/e)	Ion *2* (m/e)	Ion *3* (m/e)	Ion *4* (m/e)	Ion *5* (m/e)	Ion *6* (m/e)
IIa	161 (97%)	105 (67.5%)	77 (100%)	118 (73%)	91 (47%)	—
IIb	191 (100%)	135 (99%)	107 (10%)	148 (31%)	—	120 (8%)
IIc	195 (100%)	139 (76 5%)	111 (74%)	152 (95%)	125 (50%)	—
IId	206 (100%)	150 (20%)	—	163 (98%)	—	135 (20%)

Compound	Ion *7* (m/e)	Ion *8* (m/e)	Ion *9* (m/e)	Ion *10* (m/e)	Ion *11* (m/e)	Ion *12* (m/e)	Ion *13* (m/e)
IIe	251 (84%)	195 (39%)	178 (100%)	150 (22 [illegible])	165 (36%)	231 (18%)	206(6%)

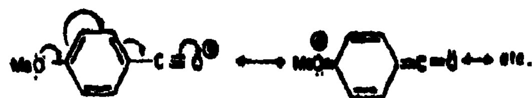
Note : The relative abundances of the ions are given in brackets The relative abundance of the base peak has been arbitrarily taken as 100%

The fragmentation of 2-amino-5-phenyl-1,3,4-oxadiazole derivatives is initiated mainly by two schemes indicated by path 'A' and path 'B' in Scheme 2. The path 'A' involving the cleavage at the bonds $O-C_2$ and C_5-N_4 leads to the formation of the benzoyl ion *2*. The path 'B' on the other hand involves the cleavage at $O-C_2$ and C_2-N_3 thereby giving the ion *4*.

Our results indicate that while the mass spectral fragmentation of the compounds IIa–d follows a similar pattern, compound IIe fragments by a slightly different mechanism. Scheme 2 depicts the mass fragmentation of the compounds IIa–d while the Scheme 3 shows the mass fragmentation of the compound IIe.

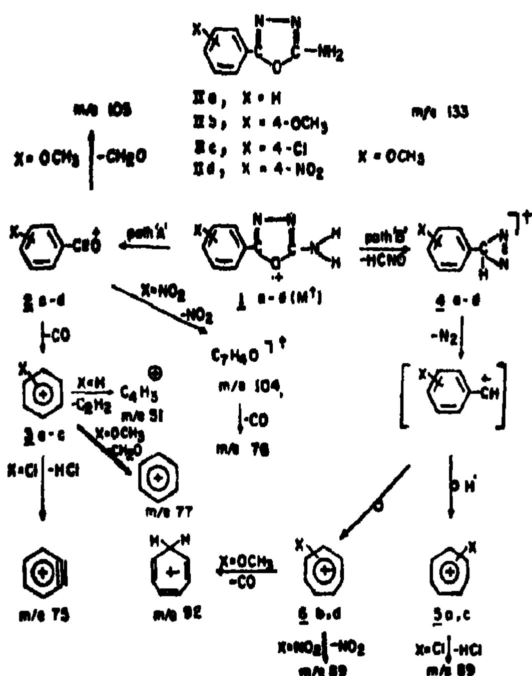
The molecular ion usually forms the base peak except in the case of IIa and IIe. In the case of the former, the ion at m/e 77 forms the base peak while in the case of the latter, the base peak appears at m/e 178.

The relative abundances of the ions *2* and *4* (Table 2) indicate that the electronic nature of the substituent group in the phenyl ring affects the mode of initial fragmentation, i.e. path 'A' or path 'B'. In the case of IIb (X=4-MeO), ion *2b* (m/e 135) is more intense (99%) but in the case of compounds IIc (X=4-Cl) and IId (X=4-NO_2), the ions *4c* (m/e 152, 95%) and *4d* (m/e 163, 98%) respectively are formed preferentially. It shows that an electron-withdrawing substituent makes, as expected, the cleavage of $O-C_5$ bond comparatively more facile thereby making the path 'B' a preferential mode of fragmentation. The ion *2b* on the other hand is greatly stabilized, as shown below, by resonance.

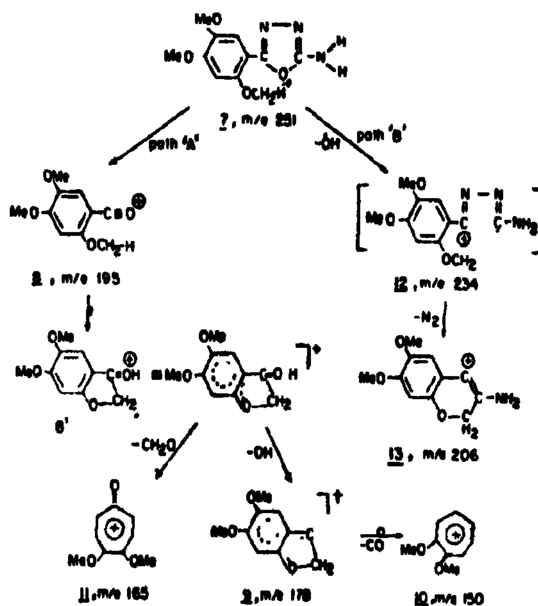


The ion *2* usually eliminates CO to form ion *3* which undergoes further fragmentation, as shown in Scheme 2, to give other important peaks in the spectrum. In the case of *2b*, fragmentation may also occur at methoxy group accompanied by the loss of formaldehyde to give the benzoyl cation at m/e 105. It appears that in *2d*, the loss of NO_2 precedes the loss of CO to give the ion at m/e 104. The latter then loses CO to give the ion at m/e 76.

The ion *4* undergoes further fragmentation accompanied by the loss of a nitrogen molecule. The resulting ion undergoes rearrangement with or without the abstraction of a hydrogen atom to form the ion *5* or the radical ion *6*, respectively. In the



Scheme 2



Scheme 3

case of IIb, a strong peak appears at m/e 133 also, which may be attributed to the process involving loss of CH_3 from the ion *4b*. The ions *5* and *6* undergo further fragmentation leading to the formation of other important ions as shown in Scheme 2.

As pointed out earlier, the compound IIe fragments in a slightly different manner. The presence of three electron releasing methoxy groups in the phenyl ring makes $O-C_5$ bond quite resistant to cleavage and therefore path 'A' (Scheme 3) becomes the preferred mode of fragmentation. This leads to the formation of trimethoxybenzoyl cation *8* at m/e 195. As pointed out earlier, the peak at m/e 178 forms the base peak in the spectrum. It appears that this ion (m/e 178) results from the loss of hydroxide radical from ion *8*. This process involves the migration of a hydrogen from *ortho*-methoxy group on to the carbonyl oxygen followed by the loss of hydroxide radical. The extensive delocalization of the ionic charge in *9* makes it quite stable and therefore, it forms the base peak in the spectrum. The ion *9* may lose CO to give the ion *10* at m/e 150. The ion *8* may also split off formaldehyde to give the ion *11* at m/e 165. It appears that a minor process involving the loss of a hydroxide radical from the parent ion *7* competes with the above described path 'A'. This process has been designated as path 'B' in Scheme 3. This also involves the migration of a hydrogen from *ortho*-methoxy group on to the carbonyl oxygen followed by the loss of hydroxide radical. The resulting ion *12* (m/e 234) splits off nitrogen molecule to form the ion *13* at m/e 206.

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Physico-chemical Studies of 1,5-Dimethyl- and 1,5-Diphenyl-1,3,5-pentanetriones with VO(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and UO_2(II)†

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The compositions of metal complexes formed by 1,5-dimethyl- and 1,5-diphenyl-1,3,5-pentanetriones with VO(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and UO_2(II) in dioxan-water mixture (50% v/v) have been determined potentiometrically at $30\pm0.1°$ in presence of sodium chloride. It was concluded from this study that 1,5-dimethyl-1,3,5-pentanetrione (H_2DAA) acts as a monobasic and 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA) as a dibasic acid.

THOUGH 1, 5 - dimethyl - 1, 3, 5 - pentanetrione (H_2DAA) was synthesised by Collie *et al*[1] in 1922, not much work has been noticed till 1960. After 1960, β,δ-triketones have been subjected to many investigations. Fernelius *et al*[2] determined the formation constants of 1-phenyl-1,3,5-hexanetrione and 1,5-diphenyl-1,3,5-pentanetrione with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(II) and reported the formation of mononuclear 1 : 1 and 1 : 2 complexes. However, Lintvedt and co-workers[3-7] have isolated homobimetallic complexes with H_2DBA with first row transition metal ions. Preliminary studies, of Fernelius appeared to be incorrect, as there are several possibilities through which coordination can occur which may lead to polynuclear complexation. In the present communication we report the compositions and stoichiometries of various metal complexes formed in the aforesaid system.

Experimental

The ligands H_2DAA and H_2DBA were prepared by standard methods[1,8]. Peroxide-free distilled dioxan was obtained by the literature method[9]. Metal salts (B.D.H., A.R.) solutions were standarised by EDTA[10]. Dioxan-water mixture (50% v/v) was prepared by adding 500 ml of deionised water to 500 ml dried and distilled dioxan. This mixture was used for preparing metal salt, ligand and sodium chloride solutions. The ionic strength was maintained constant (μ=0.01*M*) with sodium chloride solution as mentioned below:

(i) 0.002*M* Ligand (10 ml) (*a* or *a*′)+0.01*M* NaCl (10 ml)+dioxan-water (30 ml; 50% v/v),

(ii) 0.002*M* Ligand (10 ml) (*a* or *a*′)+0.002*M* Metal (10 ml) (A–G) +0.01*M* NaCl (10 ml) + dioxan-water (20 ml; 50% v/v),

(iii) 0.002*M* Ligand (15 ml) (*a* or *a*′) +0.002*M* Metal (10 ml) (A–G) +0.01*M* NaCl (10 ml) +dioxan-water (15 ml, 50% v/v), and

(iv) 0.002*M* Ligand (20 ml)(*a* or *a*′) +0.002*M* Metal (10 ml) (A–G)+0.01*M* NaCl (10 ml)+dioxan-water (10 ml; 50% v/v).

(A) denotes VO^{++}, (B) Cr^{+++}, (C) Mn^{++}, (D) Co^{++}, (E) Ni^{++}, (F) Cu^{++}, (G) UO_2^{++}, *a*, H_2DAA ligand and *a*′, H_2DBA ligand solutions.

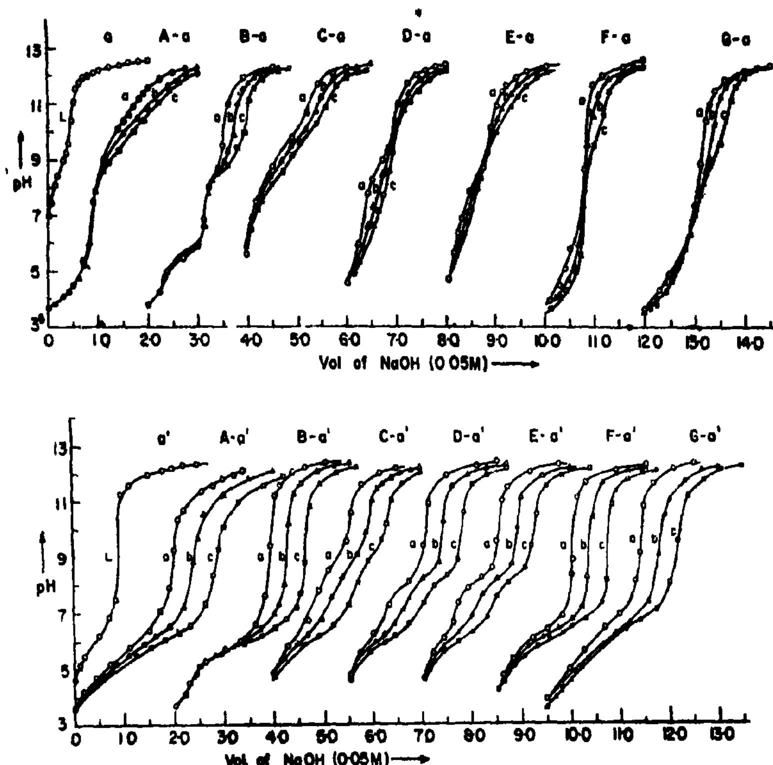
Potentiometric titrations were carried out with Digital *p*H meter (*p*H-5651 ECIL, Hyderabad) equipped with a combined glass and saturated calomel electrodes. All solutions were thermostated at $30\pm0.1°$ prior to titration. The volume of each set of solutions was kept constant (50 ml) as given in systems (i) to (iv) and separately titrated with sodium hydroxide (0.05*M*) in an oxygen-free nitrogen atmosphere. The change in *p*H was recorded as a function of volume of $[OH^-]$ added and graphs were plotted for different sets of solutions.

Results and Discussion

The solutions of the ligands H_2DAA (*a*) and H_2DBA (*a*′) when titrated with NaOH (0.05*M*) show one inflection corresponding to one and two moles of sodium hydroxide respectively, indicating mono- and dibasic behaviour of *a* and *a*′. Also, H_2DAA is a weaker acid than H_2DBA. The former is therefore expected to form stronger complexes than H_2DBA, with transition metals. The keto and enol forms were recently determined using the nmr[11].

In curves A–a, F–a and G–a only one inflection point corresponding to two moles of $[OH^-]$ at

† Dedicated to Prof. R. C. Mehrotra on his sixtieth birthday.



pH 8.0 has been observed when the solution, metal-ligand composition, of (ii) was titrated indicating the presence of [M(DAA)] species (where $M=VO^{2+}$, Cu^{2+} or UO_2^{2+}). However, with the molecular framework model three or four co-ordinated copper (with one water molecule) with DAA is unlikely as it involves considerable strain, but the species $[Cu_2(DAA)_2]$ involving square planar structure is more likely. Further in the systems (iii) and (iv) only one inflection corresponding to two moles of $[OH^-]$ at pH 8.0 was noticed, indicating the formation of aquated $[M_2(DAA)_2(H_2DAA)]$ and $[M(HDAA)_2]$ species, respectively [where M=VO (II), Cu(II) or UO_2(II)]. In all the cases the complex precipitated at pH$\simeq$11.00.

In case of Cr – H_2DAA system, the curve B – a shows three inflection points corresponding to one, three and four moles of $[OH^-]$, respectively. The curves also show the liberation of one and three protons from the ligand in the solutions of systems (ii), (iii) and (iv). However, separation of the curves occur only after pH 8 is attained. Liberation of a single proton from the ligand generates the species like $[Cr(HDAA)]^{2+}$ or $[Cr_2(HDAA)_2]^{4+}$, while the liberation of three protons accounts for the formation of [Cr(DAA)OH] or $[Cr_2(DAA)_2(OH)_2]$. The liberation of four protons in 1 : 1 mixture generates anionic complex of the type $[Cr_2(DAA)_2(OH)_4]^{2-}$. In 2 : 3 and 1 : 2 mixtures nine and five moles of $[OH^-]$ were consumed, accounting for the formation of $[Cr_2(DAA)_3(OH)_3]^{2-}$ and $[Cr(DAA)_2OH]^{2-}$.

The curve C – a shows some interesting features, as there are two inflection points for each set of compositions. Two inflection points are noted for composition (ii), one at pH$\simeq$ 9 and the other at pH $\simeq$11, corresponding to one and three moles of $[OH^-]$, respectively. Two complexes $[Mn(HDAA)_2]$ and the other anionic species $[Mn(DAA)OH]^-$ appear to be formed. Further, the curve C – a corresponding to the composition (iii) shows two inflection points at pH$\simeq$ 9 and at pH$\simeq$ 11 corresponding to 1.5 and 3.5 moles of $[OH^-]$ pertaining to the neutral $[Mn_2(HDAA)_2]$ and the anionic species, $[Mn_2(DAA)_3(OH)]^{2-}$, respectively. In the same curve pertaining to the composition 1 . 2 two inflection points corresponding to two and four moles of $[OH^-]$ are noted and the species, $[Mn(HDAA)_2]$ and $[Mn(HDAA)_2(OH)_2]^{2-}$ are assigned.

The curves D – a and E – a for the composition (ii) show two sharp inflections at pH$\simeq$7 and $\simeq$10 corresponding to one and two moles of NaOH respectively indicating the formation of 1 : 2 complex $[M'(HDAA)_2]$ at pH$\simeq$7 and 1 : 1 complex $[M'_2(DAA)_2]$ at pH$\simeq$10 [M'=Ni(II) or Co(II)]. It is therefore surprising that Co^{2+} and Ni^{2+} prefer to bind with two ligands at lower pH in which each ligand molecule behaves as monobasic ligand. At higher pH the second proton from the ligand is removed forming thereby $[M'_2(DAA)_2]$. This is contrary to what has been observed for Cu^{2+}. The compositions for the systems (iii) and (iv) show the behaviour similar to Cu^{2+} system, forming the

complexes of the types $[M'_2(DAA).H_2DAA]$ and $[M'(HDAA)_2]$, respectively. In each case two protons were liberated in two different metal-ligand compositions.

The curves A – a' and G – a' show the consumption of five moles of $[OH^-]$, thereby indicating the formation of seven coordinated $[VO(DBA)(OH)_3]^{3-}$ and eight coordinated $[UO_2(DBA)(OH)_3]^{3-}$, respectively. While in systems (iii) and (iv) parallel nature of the curves show that excess of ligand is being titrated.

In the curve B – a' (ii), five moles of $[OH^-]$ have been consumed, indicating thereby the formation of the anionic species, $[Cr(DBA)(OH)_3]^{3-}$. For other metal-ligand composition excess ligand is titrated as indicated by the parallel nature of the curve.

However, in Mn^{2+}, Co^{2+} and Ni^{2+} systems, two inflection points in their respective curves (C – a', D – a' and E – a') show two-step complexation. First inflection point between *p*H 6-9 corresponding to two moles $[OH^-]$, shows the formation of the species [M(DBA)] or $[M_2(DBA)_2]$, which further coordinates to two moles of $[OH^-]$ to form a octahedral homo-bimetallic anionic species of the type $[M(DBA)(OH)_2]^{2-}$ or $[M_2(DBA)_2(OH)_4]^{4-}$ (where $M = Mn^{2+}$, Co^{2+} or Ni^{2+}). The different inflection points for other metal-ligand compositions viz., (iii) and (iv) are, in all the cases, due to the excess of ligand which is being titrated.

Finally in curve F – a' the inflection point for metal-ligand composition (ii) corresponding to four moles of $[OH^-]$ indicate the formation of anionic species $[Cu(DBA)(OH)_2]^{2-}$ or $[Cu_2(DBA)_2(OH)_4]^{4-}$, while in systems (iii) and (iv) the curves are also parallel which indicate that excess of ligand is being titrated.

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Some Reactions of Nickel Chloride in N,N-Dimethylformamide (DMF)

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Nickel chloride forms a 1 : 3 adduct with DMF (N,N-Dimethylformamide). Some of its reactions in DMF medium have been studied with silver nitrate, potassium thiocyanate and iodide, tri- and diethyl ammonium chloride and dimethylglyoxime. Instead of a metathetical reaction a complex formation reaction occurs with silver nitrate. Complex formation and metathetical reactions also occur with the others. With bases like tri- and diethylamine, α-picoline and pyridine base displacement reactions have been found to take place. These reactions have been found to throw light on the mode of ionisation of nickel chloride in DMF. Mostly, the results have been deduced by conductometric methods.

N,N-DIMETHYLFORMAMIDE (DMF) as a polar solvent and as a medium of reactions has been studied in recent years[1-21] and has evoked considerable interest. The present investigation deals with some reactions of nickel chloride using DMF as a reaction medium. Nickel chloride is soluble in DMF and forms a solvate having the composition $NiCl_2.3HCON(CH_3)_2$ which has been isolated. Its reactions with other soluble compounds in DMF, such as silver nitrate, potassium thiocyanate and iodide, and dimethylglyoxime have been studied. It was expected that metathetical reactions resulting in the precipitation of sparingly soluble compounds in DMF viz., silver chloride and potassium chloride might result but actually the complex formation reactions also accompany them. It was also worth interesting to investigate the reactions of bases like tri- and diethylamine, α-picoline and pyridine on nickel chloride in DMF in view of an interesting solvolytic reaction with bismuth trichloride[21] in an earlier studies. However, such solvolytic reaction has not been found to occur with nickel chloride. On the other hand, only a base displacement reaction takes place.

The behaviour of these reactions has evoked interest in the mode of ionisation of nickel chloride in DMF. Among the various possibilities, the most probable mechanism is the ionisation of dimeric nickel chloride in DMF as shown below :



$$[NiCl_2]_2 \rightleftharpoons [NiCl]^+ + [NiCl_3]^- \text{ (Solvated with DMF)}$$

Experimental

Purification of solvent and bases : Dimethyl formamide and bases such as triethylamine, diethylamine, α-picoline and pyridine (all B.D.H.) were purified as described in earlier studies[22-25].

Nickel chloride adduct with dimethylformamide : 35 g of anhydrous nickel chloride was dissolved in excess of DMF (150 ml). The excess of the solvent was removed under reduced pressure. Yellow solid of the adduct was obtained. The crystals were washed with dry carbon tetrachloride and then with dry ether. The ether was finally removed under reduced pressure. The adduct was quite stable at ordinary temperature. The solid decomposed (turns black) at 68°. The composition of the adduct was found to correspond to $NiCl_2.3HCON(CH_3)_2$.Anal. Calcd. ; Ni, 16.83 ; Cl, 20.34 ; N, 12.04. Found : Ni, 16.78 ; Cl, 20.12 ; N, 11.85%.

Conductivity bridge and cell : The conductivity bridge and cell were the same as used in earlier studies[22,23].

Conductivity titrations : Conductometric titrations were performed in the usual manner and the conductance after applying volume corrections was plotted against the molar ratio (titrant/titrated substance).

Isolation of the nickel chloride adducts with bases : Anhydrous nickel chloride (5 g) was dissolved in 20 ml of purified base such as triethylamine, diethylamine, α-picoline or pyridine and the excess of the base removed under reduced pressure. Pale yellow coloured solids were obtained in all four cases. These were washed with dry carbon tetrachloride and then with dry ether. The ether was finally removed under reduced pressure. The samples were analysed and found to correspond to $NiCl_2.3B$. The analysis is given in Table 1.

Methods of analysis : In the above compounds nickel and chlorine were determined gravimetrically as nickel dimethylglyoximate and silver chloride respectively and nitrogen was determined by the Kjeldahl's method.

TABLE 1

Compound	Theoretical(%)			Found(%)		
	Ni	Cl	N	Ni	Cl	N
$NiCl_2.3(C_2H_5)_3N$	13.56	16.41	9.70	13.48	16.10	9.61
$NiCl_2.3(C_2H_5)_2NH$	16.83	20.34	12.40	16.75	20.01	12.03
$NiCl_2.3C_4H_9N$	14.86	17.37	10.25	14.96	17.12	9.95
$NiCl_2.3C_5H_5N$	16.01	19.36	11.45	15.90	19.30	11.12

Results and Discussion

Nickel chloride is exceedingly soluble in DMF and forms 1 : 3 adduct with DMF corresponding to $NiCl_2 : 3HCON(CH_3)_2$. Its reactions with silver nitrate, potassium thiocyanate, potassium iodide, triethyl ammonium chloride, diethyl ammonium chloride, dimethylglyoxime and some bases using DMF as a solvent medium are described below. The discussion is based mainly on the evidence derived from conductance measurements.

Reaction with silver nitrate : Silver nitrate dissolves readily in DMF and gives a white precipitate of silver chloride with a solution of nickel chloride in DMF. However, in presence of excess of nickel chloride the precipitate of silver chloride does not appear until one mole of silver nitrate per mole of nickel chloride has been added, probably due to the formation of a soluble complex $Ag^+[NiCl_2NO_3]^-$. The actually isolated compound was found to be $Ag[NiCl_2.NO_3].3DMF$. [Nickel chloride solution dissolves solid potassium chloride quantitatively in 1 : 1 molar ratio whereas potassium chloride is sparingly soluble in DMF. This indicates the formation of $KNiCl_3$ which is further supported by the conductometric titration curve (Fig. 1). The compound actually isolated corresponds to $KNiCl_3.3DMF$]. The conductometric titration curve (Fig. 2) of the reaction of nickel chloride with silver nitrate in DMF indicates two breaks,

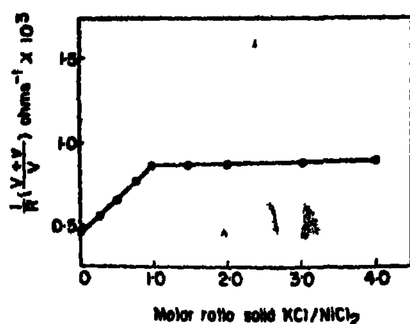


Fig. 1. Conductometric titration of 20.0 ml of 0.05*M* $NiCl_2$ with solid KCl in DMF.

one at 1 : 1 molar ratio and the other at 1 . 2 molar ratio. The latter break indicates that all the two chloride ions present in the nickel chloride molecule are precipitated as silver chloride. This is also confirmed by weighing of silver chloride obtained with excess of silver nitrate. The former

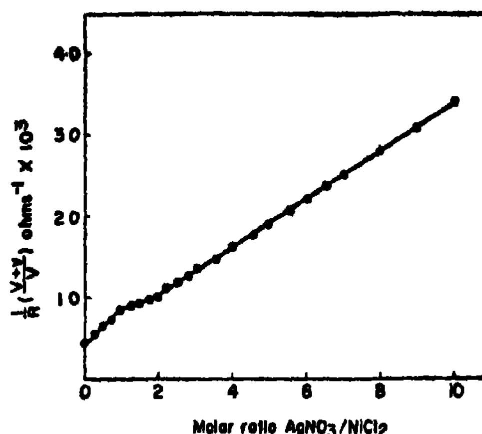
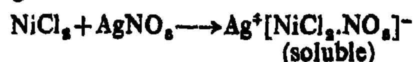


Fig 2. Conductometric titration of 20.0 ml of 0.05*M* $NiCl_2$ with 1.0*M* $AgNO_3$ in DMF.



break at 1 : 1 molar ratio can be explained by the following reaction :

$$NiCl_2 + AgNO_3 \longrightarrow Ag^+[NiCl_2.NO_3]^- \text{ (soluble)}$$

Reactions with tri- and diethyl ammonium chloride : Conductometric titration of nickel chloride with tri- and diethyl ammonium chloride shows a break at 1 . 1 molar ratio indicating the formation of $NiCl_3^-$ ion (Fig. 3). The solution remains clear. Further the compounds $(C_2H_5)_3NH^+[NiCl_3.3DMF]^-$ and $(C_2H_5)_2NH_2^+[NiCl_3.3DMF]^-$ were actually isolated by mixing equal volumes of equimolar solutions of tri- and diethyl ammonium chloride and nickel chloride in DMF, and then

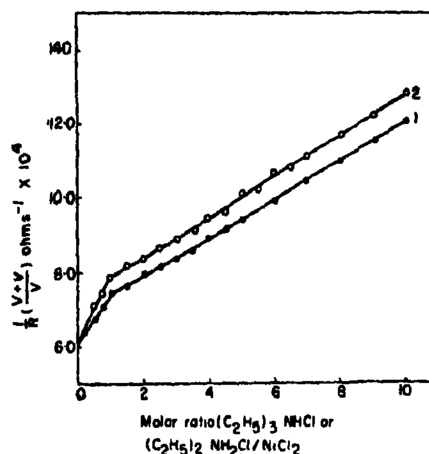


Fig. 3. Curve 1 : Conductometric titration of 20.0 ml of 0.005*M* $NiCl_2$ with 0 1*M* $(C_2H_5)_3NHCl$ in DMF.
Curve 2 : Conductometric titration of 20.0 ml of 0.005*M* $NiCl_2$ with 0.1*M* $(C_2H_5)_2NH_2Cl$ in DMF.

isolating the solids after removing the solvent under reduced pressure.

Reactions with potassium thiocyanate and potassium iodide : Potassium thiocyanate and potassium

iodide are soluble in DMF to the extent of about one mole per litre. Therefore, the study of the reaction between nickel chloride and potassium thiocyanate or potassium iodide is possible in DMF. The following two possibilities were expected to occur :

(a) a metathetical reaction resulting in the precipitation of KCl as it is sparingly soluble in DMF, and

(b) a complex formation reaction.

It has been observed that actually both categories of reactions viz., metathetical and complex formation reactions, take place when potassium thiocyanate or potassium iodide is mixed with nickel chloride in DMF. Initially no precipitate of KCl appears but it is visible after two moles of KSCN or KI for one mole of nickel chloride have been added. The reactions have been followed conductometrically and two breaks occur (Fig 4)

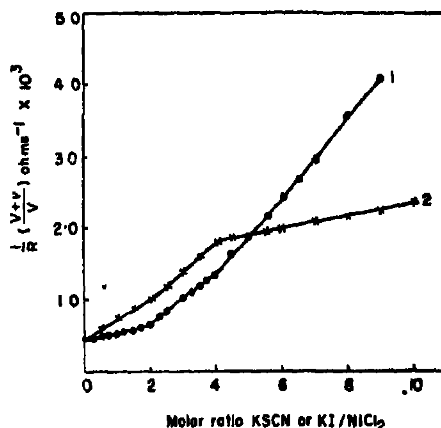


Fig. 4. Curve 1 : Conductometric titration of 20 0 ml of 0.05*M* $NiCl_2$ with 1.0*M* KSCN in DMF.
Curve 2 : Conductometric titration of 20 0 ml of 0.05*M* $NiCl_2$ with 1.0*M* KI in DMF.

viz., (i) at two moles which can be explained by the following equations :

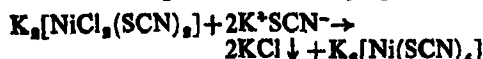


$$NiCl_2 + 2K^+SCN^- \longrightarrow K_2[NiCl_2(SCN)_2]$$

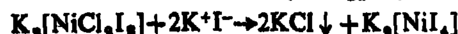


$$NiCl_2 + 2K^+I^- \longrightarrow K_2[NiCl_2I_2]$$

and (ii) at four moles. The latter break can be explained with the help of the following equations :



$$K_2[NiCl_2(SCN)_2] + 2K^+SCN^- \rightarrow 2KCl\downarrow + K_2[Ni(SCN)_4]$$



$$K_2[NiCl_2I_2] + 2K^+I^- \rightarrow 2KCl\downarrow + K_2[NiI_4]$$

Reactions with dimethylglyoxime : Dimethylglyoxime is insoluble in water. Its alcoholic solution is therefore used for the very well known reaction of nickel chloride and dimethylglyoxime in aqueous medium. When alcoholic dimethylglyoxime solution is mixed with an aqueous solution of nickel chloride, red precipitate of nickel dimethylglyoximate is formed. The reaction has

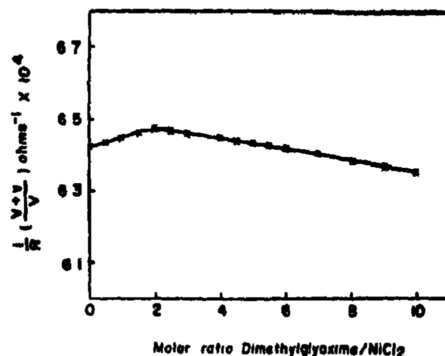
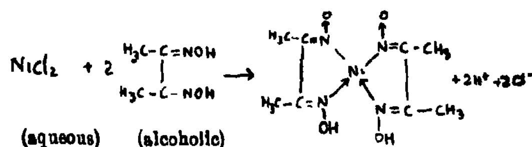


Fig 5. Conductometric titration of 20.0 ml of 0.005*M* $NiCl_2$ with 0 1*M* dimethylglyoxime(alcoholic) in aqueous medium.

been followed conductometrically and a break at 1 2 molar ratio of nickel chloride and dimethylglyoxime has been observed (Fig. 5). The reaction can be explained with the following reaction :



Dimethylglyoxime is soluble in DMF to the extent of about 0.1 mole/litre. Therefore, the study of the reaction between nickel chloride and dimethylglyoxime is possible in a single pure solvent. It was expected that a chelate formation reaction analogous to that observed in aqueous medium may take place. However, it has been observed experimentally that a precipitate of nickel dimethylglyoximate does not appear in DMF medium and the solution remains clear even with excess of dimethylglyoxime solution. The conductomertric titration curve (Fig. 6) of the reaction

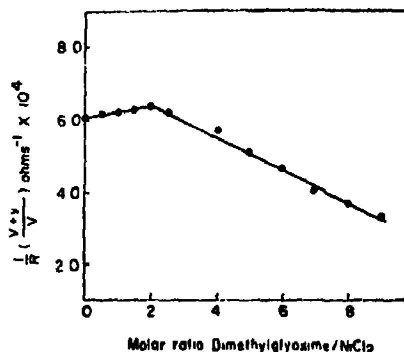
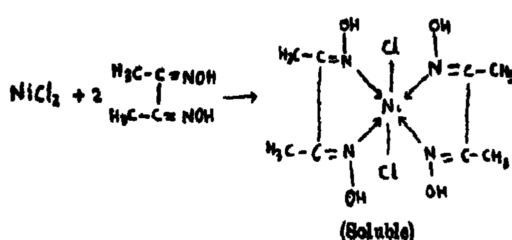


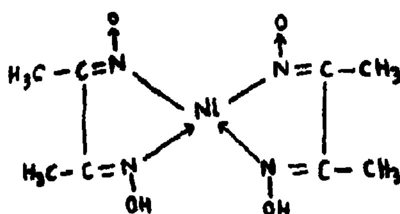
Fig. 6. Conductometric titration of 20.0 ml of 0.005*M* $NiCl_2$ with 0.1*M* dimethylglyoxime in DMF.

of nickel chloride and dimethylglyoxime in DMF shows a break at 1 : 2 molar ratio and the break

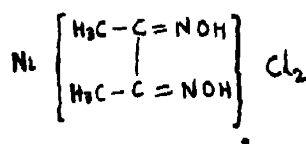
can be explained with the help of the following reaction :



When the mixture of nickel chloride and dimethylglyoxime in DMF is treated with bases such as triethyl amine or diethyl amine, a red precipitate is obtained and this precipitate is insolnble in DMF indicating the formation of the following complex :



This type of reaction has also been studied conductometrically after preparing



by mixing nickel chloride and dimethylglyoxime in 1:2 molar ratio in DMF and then titrating the mixture with triethylamine (Fig. 7). The conductance increases and a break is observed at 1 : 2 molar

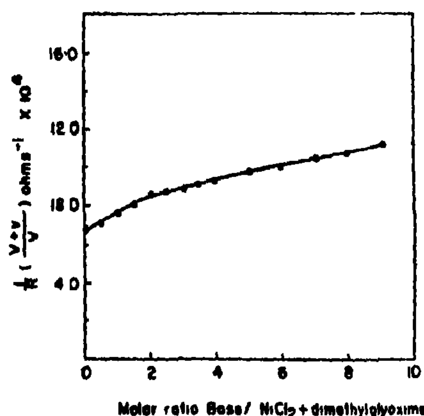
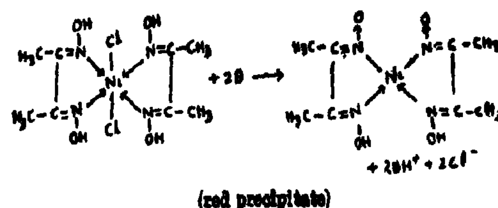


Fig. 7. Conductometric titration of 20.0 ml of 0.005M $NiCl_2$+2.0 ml of 0.1M dimethylglyoxime with 0.1M triethylamine in DMF.

ratio. A red precipitate of nickel dimethylglyoximate is formed during the reaction. The break can be explained by the following equation :



The reagent dimethylglyoxime cannot be titrated with the base in DMF.

Reactions with bases : When the solution of nickel chloride in DMF is treated with bases such as triethylamine, diethylamine, α-picoline and pyridine, the solution remains clear even with excess of base. Conductometric titration curves give a sharp break at 1 : 3 molar ratio (Fig. 8). The

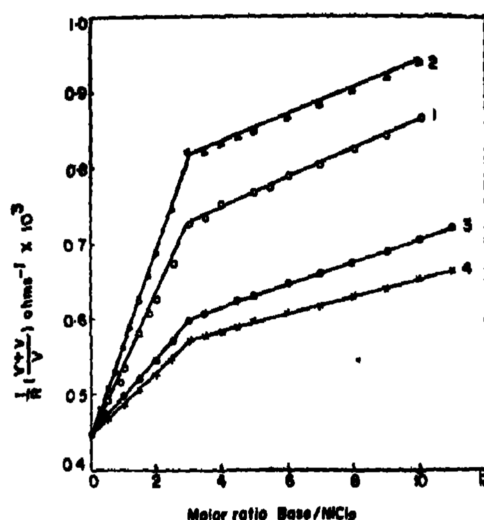
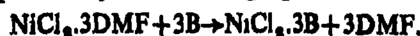


Fig. 8. Curve 1. Conductometric titration of 20.0 ml of 0.05M $NiCl_2$ with 1.0$M$$(C_2H_5)_3N$ in DMF.
Curve 2. Conductometric titration of 20.0 ml of 0.05M $NiCl_2$ with 1.0M $(C_2H_5)_2NH$ in DMF.
Curve 3 : Conductometric titration of 20.0 ml of 0.05M $NiCl_2$ with 1.0M C_6H_7N(α-picoline) in DMF.
Curve 4 : Conductometric titration of 20.0 ml of 0.05M $NiCl_2$ with 1.0M C_5H_5N in DMF.

reaction is a base displacement and may be explained by the following equation :



$NiCl_2.3DMF+3B \rightarrow NiCl_2.3B+3DMF.$

Nickel chloride has also been reacted with the bases such as triethylamine, diethylamine, α-picoline and pyridine separately and directly without the presence of DMF. The isolated compounds have been found to correspond to $NiCl_2.3B$.

Mode of ionization of nickel chloride in DMF medium : The conductance of nickel chloride in DMF is (0.05M solution has sp. conductance 0.48×10^{-3}) much larger in comparison to that of the solvent and hence it is deduced that nickel chloride should ionize in some manner in DMF.

There are following possibilities viz., (i) $NiCl_2 \rightleftharpoons Ni^{2+} + 2Cl^-$, (ii) $NiCl_2 \rightleftharpoons NiCl^+ + Cl^-$, (iii) $2NiCl_2 \rightleftharpoons$ (solvated) (solvated) $NiCl^+ + NiCl_3^-$ and (iv) $2NiCl_2 \rightleftharpoons Ni^{2+} + NiCl_4^{2-}$. (solvated) (solvated)

The formation of highly charged ions in a solvent of relatively low dielectric constant would not seem probable as they would tend to form ion pairs and so the possibility of nickel chloride in DMF to ionise as suggested by (i) and (iv) are considered improbable. The molar conductance of nickel chloride in DMF is 62.7 $ohm^{-1}cm^2mol^{-1}$ at 25°. It is even less than the order of the other 1 : 1 electrolytes whose conductance has been determined in DMF. This is further supported by the fact that Shedlovsky's equation[24], when applied to the above system according to equation (iii) and considering nickel chloride as a dimer gives a straight line (Fig. 9) when $\frac{1}{\Lambda s}$ is plotted against $c\Lambda sf_\pm^2$ Shedlovsky's equation holds good for 1 : 1 electrolytes and since it is applicable to the above system, it may be deduced that during ionization two ions should be produced from one molecule. The mode of ionization mentioned under (iii) may fulfil the condition of Shedlovsky's plot when nickel chloride behaves as a dimer.

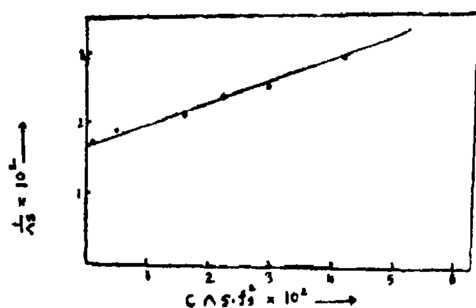


Fig 9. $NiCl_2$

The composition of adduct of nickel chloride with DMF viz., $NiCl_2$ 3DMF clearly indicates that it is not a monomer, because the usually accepted coordination number of nickel is either four or six. If nickel chloride was to be a monomer, it should have two or four moles of DMF attached to it. If dimer or trimer formulae of nickel chloride are written and the six coordination number of nickel is satisfied by attaching DMF molecules to the nickel atoms, then as shown in Fig. 10 the dimer will have the composition $[NiCl_2]_2$ 6DMF and the trimer will have the composition $[NiCl_2]_3$ 10DMF or $[NiCl_2]_3$.8DMF.

The actual composition corresponds to the dimer and hence the dimeric nature of nickel chloride DMF adduct in the solid state may be reasonably assumed.

In view of the above consideration the most probable mode of ionization is as suggested under (iii) viz.,



$$[NiCl_2]_2 \rightleftharpoons NiCl^+ + NiCl_3^-$$
solvated solvated

The mode of ionization under (ii) is not likely in view of the fact that it would require nickel chloride DMF adduct to be a monomer. Further, the formation of $[NiCl_3]^-$ ion (*loc. cit.*) support the above suggested mode of ionization for the nickel chloride in DMF.

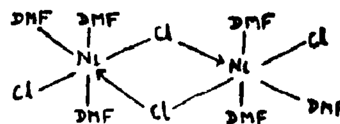


Fig 10 (a) Dimer $(NiCl_2)_2$ 6DMF

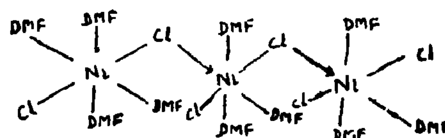


Fig 10 (b) Trimer, $(NiCl_2)_3$ 10DMF

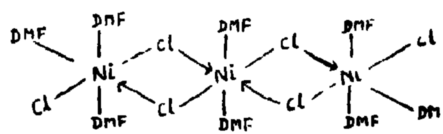


Fig 10 (c) Trimer $[NiCl_2]_3$ 8DMF

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Reductive Alkylation of 2-Methyl-1,4-Naphthaquinone (Menadione) at Mercury Pool Cathode$^{\varphi}$

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The electrochemical reduction of 2-methyl-1,4,-naphthaquinone (I) dimethyl formamide (DMF) in presence of alkylating agents (organic halides) and different supporting electrolytes, leads mainly to the formation of 1,4-dialkyl ethers of naphthalene – the 0-alkylated products. The reductive alkylation with ethyl bromide as alkylating agent, however, affords oxygen as well as carbon alkylated products, the higher yield of C-alkylation has been observed using LiCl as supporting electrolyte. Polarization, polarographic and cyclic voltammetric studies of (I) have been made and a plausible mechanism for ether formation has been suggested.

2-METHYL-1,4-NAPHTHAQUINONE (I) is related to vitamin K and is a biologically active substance. Mann and Barnes have briefly reviewed[1] the general electrochemistry of quinones. Fujinaga *et al*[2] have studied the electrochemical reduction of naphthaquinones in various aprotic solvents. Quinones with high redox potentials have been reductively methylated with dimethyl sulphate in the presence of pyridine[3]. The selective methylation of 2-methyl-1,4-naphthaquinol to 2-methyl-1,4-dimethoxy naphthalene has been reported by Clinton *et al*[4], employing usual chemical method. Anodic methoxylation of naphthalene as well as 1- and 2-methoxynaphthalene has also been reported by Bockmair and coworkers[5]. Two-one electron polarographic reduction of a number of quinones in aprotic media have been determined by Peover *et al*[6,7]. Recently there have been great synthetic interest on the electrochemical reductive alkylation of a number of diketones[8] and quinones[9]. In the present communication we describe the electrochemical reductive alkylation of 2-methyl-1,4-naphthaquinone in DMF at mercury pool cathode. Tetrabutyl ammonium bromide (TBAB) and lithium chloride have been used as supporting electrolyte.

Experimental

Materials : 2-Methyl-1,4-naphthaquinone, m.p. 106° (Sigma); lithium chloride (Sisco), ethyl bromide (Riedal); benzyl chloride (SDS) were used without further purification. Phenacyl bromide[10] and tetrabutyl ammonium bromide[11] were prepared by reported methods.

Cell assembly : A 500 ml beaker with provision to hold porous diaphragm, thermometer and magnetic stirrer was used. Mercury pool was used as a cathode (area 55.89 cm^2) and carbon plate inside the diaphragm served as anode. Polarization studies were made with reference to saturated calomel electrode.

Electrolysis and work up : Following is the detail of a typical electrolysis. Catholyte : 120 ml 2 % lithium chloride or TBAB solution in DMF containing 2 g of 2-methyl-1,4-naphthaquinone and organic halide in 1 : 2 molar ratio respectively. Anolyte 50 ml 2 % lithium chloride or TBAB solution in DMF. Details of the experiment are given in Table 1. The current was passed for theoretical time corresponding to 2F/mole. During electrolysis, the catholyte assumed a dark brownish green colour which persisted even at the end of the electrolysis. The catholyte was filtered off and DMF was stripped off at 50°/35 mm. The content was poured into distilled water and extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulphate, filtered off and the solvent was removed by distillation. The residue was chromatographed on a column of silica gel. Elution with different solvents or solvent mixture gave corresponding 1,4-diethers of 2-methyl naphthalene.

In case of the reaction with ethyl bromide, two products were obtained. The first product (IIa), a colourless solid, was isolated by eluting silica gel column with pure petroleum ether (60-80°) and petroleum ether-benzene (4 : 1) mixture, while the second product (III), an orange coloured solid, was obtained by eluting with petroleum ether and benzene (1 : 1) mixture. The yield, m.p. and spectral data of the products obtained are given in Table 2.

Polarographic and cyclic voltammetric study : A solution (10^{-4} molar) of (I) in dry DMF containing 0.1 molar tetrabutyl ammonium perchlorate (dried) was used for polarographic (Fig. 1) and cyclic voltammetric (Fig. 2) studies. Polarographic study was carried out in a three electrode system cell (Pt being counter electrode) and reduction potential was measured with reference to saturated calomel electrode. Cyclic voltammetry was carried out in

φ Dedicated to Prof. R. C. Mehrotra, my teacher, on the occasion of his 60th birthday.

TABLE 1—EXPERIMENTAL DETAILS OF REDUCTIVE ALKYLATION OF 2-METHYL-1,4,-NAPHTHAQUINONE (2 0 g) IN DMF AT MERCURY POOL CATHODE (area 55.89 cm^2, c.d. 0 0053 A cm^{-2}) TEMPERATURE 20-25°

Sl. No.	Alkylating agent (wt. in g)	Supporting electrolyte (%)	Anode	Current (A)	Cell voltage (V)	Current efficiency (%)
1.	C_2H_5Br (2.51)	lithium chloride (2)	Carbon plate	0.3	18	30+
2.	C_2H_5Br (2.51)	tetrabutyl ammonium bromide (2)	Carbon plate	0.3	56-40	30+
3.	$C_6H_5CH_2Cl$ (1.46)	tetrabutyl ammonium bromide (2)	Carbon plate	0 3	10	30.8
4.	$C_6H_5COCH_2Br$ (2.8)	lithium chloride (2)	Carbon plate	0.3	24	38.0

\+ Total current efficiency for the compound IIa and III.

TABLE 2—PHYSICO-CHEMICAL CHARACTERISTIC OF PRODUCTS IN THE REDUCTIVE ALKYLATION OF 2-METHYL-1,4-NAPHTHAQUINONE

Alkylating agent (Supporting electrolyte)	Product+ (Nature)	m.p. °C	Mass yield (%)	Characteristic ir bands (cm^{-1}) C–H	C–O–C/>C=O	$^1H_{nmr}$ δ(ppm)
EtBr (LiCl)	II_a (Colourless solid)	61	35	2820, 2880	1250, 1065	1.3-1 7(t)6H CH_3, 2.4-2.5(s) 3H Ar CH_3, 3 8-4.4(q)4H CH_2, 6.6-8.3(m)5H Ar.
	III$^{\varphi}$ (Orange solid)	272-273	42		/1660	1.5-1 6(t)3H CH_3, 1.7-1.8(t) 3H Ar CH_3, 4.3-4.4(o)2H CH_2; 7.3-8.5(m)4H Ar.
EtBr (TBAB)	II_a (Colourless solid)	61	57	2820, 2880	1250, 1065	—
	III$^{\varphi}$	272-273	18		/1660	—
$PhCH_2Cl$ (TBAB)	II_b (Colourless solid)	235	49	—	—	2.1(s)3H Ar CH_3, 3 2(s)4H CH_2, 6.8-7.4 (m)15H Ar.
$PhCOCH_2Br$ (LiCl)	II_c (Colourless solid)	180	52	2990, 3060	1240, 1075	2 0(s)3H Ar CH_3, 2.7(s)4H CH_2, 6.6-7 4(m)15H Ar.

\+ All compounds gave satisfactory carbon and hydrogen analysis (Coleman 33 Model)

φ Absorbs at λ_{max} 280 nm.

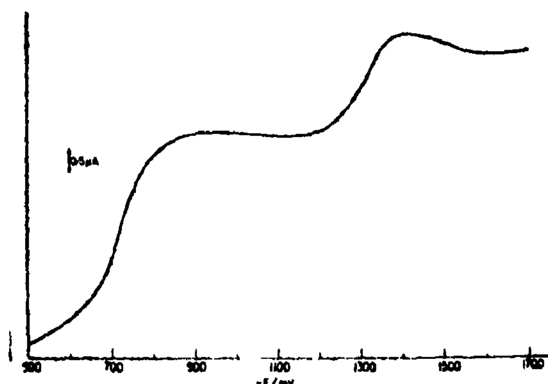


Fig. 1. A polarogram at DME 0 1*M* tetrabutyl ammonium perchlorate in DMF.

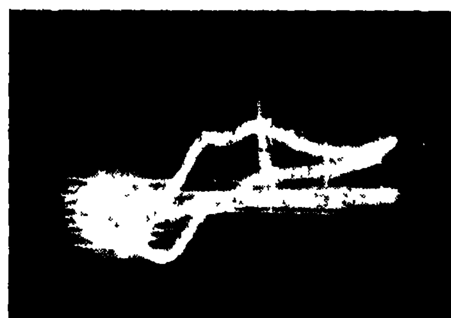


Fig 2 Cyclic voltammogram of 2-methyl-1,4-naphthaquinone (I) in DMF at scan rate 9 V/sec. (between 500-1400 mV).

the same solvent-supporting electrolyte system at a scan rate of 9 V/sec between 500-1400 mV and the signals were recorded photographically from a Tektronix oscilloscope.

Results and Discussion

The electrochemical reductive alkylation of 2-methyl-1,4-naphthaquinone proceeds smoothly at mercury pool cathode in DMF containing lithium chloride or TBAB as supporting electrolyte. Yields of corresponding diethers varies between 35-57 % (C. E. 15-38 %). Half wave potential for the polarographic reduction of 2-methyl-1,4-naphthaquinone in DMF containing 0.1 *M* tetrabutyl ammonium perchlorate used as a supporting electrolyte is consistent with a mechanism involving two-one electron steps (Fig. 1). The value of their first and second

half wave potentials are −717.5 mV (slope 85 mV) and −1300 mV (slope 58.3 mV) respectively. Both reduction steps appear to be reversible. It seems from the polarographic studies that in the solvent of low proton availability 2-methyl-1,4-naphthaquinone undergoes two-one electron polarographic reduction. The cyclic voltammetry (Fig. 2) also reveals two-one electron reduction in a reversible step (56 mV).

In the preparative study, the cathodic reduction of I was carried out at constant current (0.3 A). Polarization curves (Fig. 3) showed that maximum depolarization occurred at current density, 0.0057 A cm^{-2}.

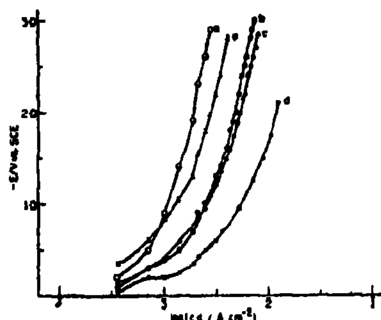
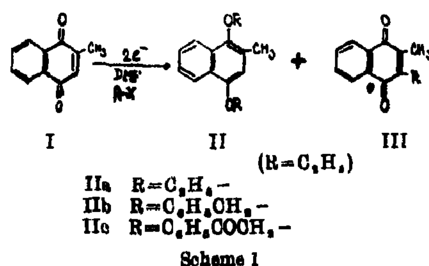


Fig. 3. Polarization studies for 2-methyl-1,4-naphthaquinone (I) at mercury pool
(a) DMF and 2% LiCl, (b) DMF, 2% LiCl and 2-methyl-1,4-naphthaquinone, (c) DMF, 2% LiCl and 2-methyl-1,4-naphthaquinone and ethyl bromide, (d) DMF, 2% TBAB, 2-methyl-1,4-naphthaquinone and benzyl chloride and (e) DMF, 2% TBAB, 2-methyl-1,4-naphthaquinone and phenacyl bromide.

The reductive alkylation of I (Scheme 1) affords mainly O-alkylated products (IIa-c). However, in case of the reaction with ethyl bromide, C-alkylated product (III) has also been isolated. While the diethers (IIa-c) are colourless compounds, the product III (C-alkylated) is bright orange coloured, indicative of retained quinonoid structure



Scheme 1

The effect of supporting electrolyte on the product distribution II and III in the cathodic reduction of I with ethyl bromide is remarkable and is given below in Table 3.

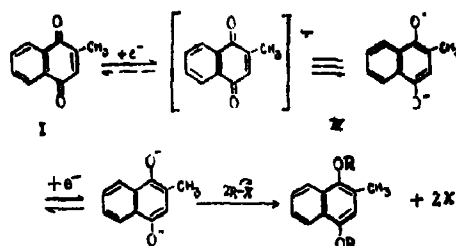
The higher yield of C-alkylated product in presence of LiCl is in conformity with an early report[6]. With benzyl chloride and phenacyl

Table 3—Effect of Supporting Electrolyte on the Product Distribution (IIa and III). The Current Density and other Parameters of Electrolysis Remaining Same

Sl. No.	Supporting electrolyte	Product yield(%) IIa	III
1.	LiCl	35	42
2.	TBAB	57	18

bromide as the alkylating agents, only the O-alkylated products (IIb and IIc respectively) were obtained. Compared to the conventional chemical methods[12-14] the electrochemical procedure reported here is easy and smooth to afford the diethers IIa-c.

During electrolysis, the catholyte developed a dark brownish green colour which persisted even at the end of the reaction. This is indicative of a possible intermediary of an anionic species. Based on the voltammetric and preparative studies the formation of 2-methyl naphthalene-1,4-diethers could possibly be represented in the following manner (Scheme 2):



Scheme 2

The C-alkylated products probably also originate from the common reaction intermediate, the anion radical IV.

Acknowledgement

Two of the authors (A. J. and A. Y.) thank U.G.C., New Delhi for Research Fellowships.

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Studies in Fluorinated 1,3-Diketones and Related Compounds—Part XIII* : Synthetic and Spectral Studies of Some New Fluorinated *Tris* Europium 1,3-Diketonates

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A number of new polyfluorinated *tris* europium 1,3-diketonates have been synthesised by treatment of appropriate polyfluorinated 1,3-diketones with europium chloride in methanol. All these compounds have been characterized by their elemental analysis and spectral studies, viz., ir, ^{1}H nmr and mass. Important absorption peaks are observed in the regions 1620-1540 cm^{-1} (C=O), 1540-1400 cm^{-1} (C=C), 1000-850 cm^{-1} (C–F).

In ^{1}H nmr, a sharp singlet at δ (6.2-6.4) ppm due to methine proton (=CH) has been observed.

POLYFLUORINATED 1,3-diketones are indispensable reagents in analytical chemistry and important recent uses are in analysing lunar samples[1], cobalt in vitamin B_{12}[2] and in the detection of other trace elements in blood, serum and other essential biological materials. Due to their excellent complex forming properties, reagents like theonyltrifluoroacetone (TTA), thiotheonyltrifluoroacetone (STTA), heptafluorobutanoylpivalylmethane (FOD) find wide applications in analytical chemistry.

After Hinckley's[3] discovery of $Eu(DPM)_3$. 2 py as nmr shift reagent, a large number of lanthanide 1,3-diketonates have been synthesized as possible nmr shift reagents. The chemical property which permits this application is the Lewis acidity, which the chelates possess, as a consequence of their coordinative unsaturation atmosphere. Chelates of fluorinated 1,3-diketones undergo much stronger interaction with nucleophiles (e.g. alcohols, amines, esters, ethers etc.) than similar non-fluorinated chelates[4]. This is due to the increased acidity[4] of the fluorinated 1,3-diketones and their increased solubility. In recent years, achiral reagents, like $Eu(FOD)_3$, have been successfully employed for determination of diastereoisomeric excess of amino acids and other biologically active compounds and a chiral nmr shift reagent, Eu(trifluoroacetyl-d-camphorato)$_3$, has been utilized to determine the enantiomeric excess in many classes of compounds[5-8].

During the last one decade, we have undertaken an extensive programme on the chemistry of fluorinated 1,3-diketones[9,10]† and related compounds and have reported the synthesis of new polyfluorinated 1,3-diketones and their metal chelates and some of their structural studies like examination of their quasiaromatic nature and electrophilic substitution reactions in such systems[11-13]. We have also utilized these compounds as reaction intermediates for the synthesis of various bioactive heterocycles[14-16].

* Part XII : K. C. Joshi, V. N. Pathak and V. Grover, *J. Fluorine Chem.*, 1981, 17, 555.

Experimental

IR spectra were recorded using a Perkin-Elmer-337 spectrometer. ^{1}H nmr spectra by a Perkin-Elmer RB-12 in $CDCl_3$ solution with TMS as an internal standard.

Synthesis of 3,4-difluoroacetophenone : A mixture of 1,2-difluorobenzene (25 g ; 0.22 mole) and anhydrous aluminium chloride (61.2 g ; 0.46 mole) was taken in a three necked flask (500 ml) fitted with a dropping funnel, mercury sealed stirrer and a reflux condenser. Acetyl chloride (15.6 g ; 0.22 mole) was gradually added with stirring The reaction mixture was refluxed for 10 hr. The residue was decomposed with ice cold hydrochloric acid (6*N* ; 150 ml) and extracted with ether, the solvent was removed and 3,4-difluoroacetophenone was dried over magnesium sulphate and distilled at 170°. Synthesis of 2,4,6-trifluoroacetophenone was done in a similar manner

Synthesis of polyfluorinated 1,3-diketones : Fluorinated 1,3-diketones were prepared by Claisen condensation reaction of the fluorinated acetophenone with fluorinated esters. Fluorine substituted acetophenone (0.1 mole) was added to an ethereal suspension of sodamide (0.2 mole) with stirring. After half an hour, an ethereal solution of fluorinated ester (0.1 mole) was added dropwise with stirring and refluxed. The reaction mixture was left overnight and then extracted with cold water. The 1,3-diketone was precipitated in the form of its copper(II) chelate by adding a hot solution of cupric acetate. The free 1,3-diketone was regenerated on treatment with 10% sulphuric acid and distilled under reduced pressure.

† Our work on fluorinated 1,3-diketones, at Jaipur, was initiated at the suggestion of Prof. R. C. Mehrotra, F.N.A., and it gives us great pleasure to dedicate this paper to him on the occasion of his 60th birthday.

TABLE 1—ANALYTICAL AND CHARACTERISTIC DATA OF *Tris* EUROPIUM 1,3-DIKETONATES

Sl. No.	Substituent in Ar	R	m.p. °C	Yield %	Molecular Formula	C% Calcd.	C% Found	H% Calcd	H% Found	F% Calcd.	F% Found
1.	3,4-DiF	CH_3	166	76	$C_{30}H_{21}O_6F_6Eu$	48.45	48.41	2 82	2 81	15.34	15.31
2.	3,4-DiF	CF_3	183	88	$C_{30}H_{12}F_{15}O_6Eu$	39 78	39 80	1.32	1.30	31.49	31.40
3.	3,4-DiF	C_6H_5	176	72	$C_{45}H_{27}O_6F_6Eu$	50.44	50 40	3.44	3.42	14.52	14.50
4.	3,4-DiF	C_2F_5	168	70	$C_{33}H_{12}O_6F_{21}Eu$	37 58	37.50	1.14	1.10	37.82	37.80
5.	3,4-DiF	C_3F_7	196	72	$C_{36}H_{12}O_6F_{27}Eu$	35 85	35 82	0.99	1 00	42.57	42.55
6.	2,4,6-TriF	CF_3	187	85	$C_{30}H_9F_{18}O_6Eu$	37.66	37.62	0.68	0.58	37 55	37 50

Synthesis of tris *europium 1,3-diketonates* : Europium chloride (0.004 mole) was dissolved in a minimal amount of methanol and added dropwise to a methanolic solution of 1,3-diketonato enolate anion (0.012 mole). The complex was precipitated by slow addition of a ten fold excess of water to the resulting methanolic solution. The precipitated *tris* europium 1,3-diketonates were crystallized from benzene. Finally, the chelates were dried in vacuum, over phosphorus pentaoxide, for 24 hr.

All *tris* europium 1,3-diketonates are recorded in Table 1 with their analytical data.

Results and Discussion

In the ir spectra, the absence of absorption peaks near 1700 cm^{-1}, in all *tris* europium 1,3-diketonates, can be taken as an evidence of all six oxygen atoms of 1,3-diketones being bonded directly to the europium ion. The chemical analysis and M^+ values in the mass spectra also support their hexacoordination. Other important peaks are at 1620 – 1540 cm^{-1} (C=O) stretching mode, 1540 – 1400 cm^{-1} (C=C) stretching mode coupled with the C – H in-plane bending mode, 1580 – 1450 cm^{-1} (C – F) stretching mode of perfluoroalkyl groups, 1000 – 850 cm^{-1} (C – F) deformation mode of perfluoroalkyl groups. The shift in C=O absorption frequency indicates that chelation is stabilized due to the benzenoid resonance effect in which europium back donates its F electrons to the ligand.

In ^1H nmr spectra, disappearance of enolic proton (=C – OH) resonance provides a strong evidence for coordination of 1,3-diketonato anion moiety with europium ion. In all ^1H nmr spectra, a sharp signal is observed at δ(6.2 - 6.4) ppm which is due to the resonance of the methine proton (=CH) of the γ-position of the chelated ring. Aromatic protons show sharp signals between δ(6.4 – 7.9) ppm.

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Role of Metal Ions in Reactions of dl-Camphorquinone with Monoamines

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The condensation of monoamines with dl-camphorquinone in the presence of metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}) gave two classes of metal complexes. The reactions leading to Class I complexes gave monoimines with the imino group at C(2) and C(3) positions. The reactions leading to Class II complexes gave monoimines with the imino group at C(3) position only, similar to that obtained by the direct condensation reaction in the absence of a metal ion. A diimine is also obtained in a reaction involving copper(II) complexes of Class I.

FORSTER[1] has noted that d-camphorquinone reacts with aniline forming an imine group only at the C(3) position, this site being sterically least hindered. However, in the condensation reaction of d-camphorquinone with *ortho*-phenylenediamine, both the carbonyl groups at C(2) and C(3) participate in an imine formation reaction yielding d-camphorquinoxaline[2]. The effect of R group (in RNH_2) on the imine formation reaction would therefore enlighten the steric details in d-camphorquinone. Further variations in the steric factors can be introduced by carrying these reactions in the presence of metal ions. In the later reactions it may be possible to separate the Schiff base complexes. This paper reports the results of study of this problem.

Experimental

Infrared spectra were measured in the range 400-4000 cm^{-1} on a Perkin-Elmer grating infrared spectrometer 337 for the nujol and hexachlorobutadiene mulls. Hydrogen-1 nmr spectra were recorded on Perkin-Elmer R-32 spectrometer at 90 MHz using $CDCl_3$ as solvent and tetramethylsilane for lock signal.

All the chemicals were of AnalaR B.D.H grade and of Aldrich Chemicals. dl-Camphorquinone was prepared by the direct oxidation of dl-camphor using Riley's selenium dioxide method[3].

Synthesis of metal complexes. All the complexes were prepared by using a similar procedure. A typical procedure for the condensation of dl-camphorquinone with aniline in the presence of nickel chloride is given below.

To a solution of nickel chloride (2.39 g ; 0.01 mole) in methanol (20 ml) was added slowly, with constant stirring, a solution of dl-camphorquinone (3.32 g ; 0.02 mole) in methanol (20 ml) and of aniline (3.72 ; 0.04 mole) in methanol (10 ml). A suspension of sodium acetate in methanol was added to this mixture with constant stirring and the mixture was refluxed on water bath for 20 hr. The mixture was brought to room temperature and was filtered. The mother liquor was reduced to a small volume *in vacuo*, and residue was extracted with *n*-hexane (extract P). The residue from this stage was extracted with benzene (extract Q). The residue from this treatment was further extracted with chloroform giving extract R. The residue from this final treatment was discarded.

The extract P was chromatographed on a neutral alumina packed column. Elution with *n*-hexane gave two fractions. The first fraction was of unreacted dl-camphorquinone and the second fraction gave the Schiff base (IIA). The elution with benzene-*n*-hexane mixture (1 4 v/v) gave the Schiff base (IIB).

The extract Q was reduced to a small volume *in vacuo* and was washed with *n*-hexane yielding the yellow crystals of *10*. The extract R was reduced to a small volume *in vacuo* and was washed with benzene yielding the yellowish-green crystals of *10a*.

During the synthesis of copper(II) complexes, the compounds obtained from extracts Q and R were further washed five to six times with diethylether.

The reactions in which α-diiminocamphor, C, was formed, the compound C was obtained in a fraction eluted with benzene-*n*-hexane (1 : 1 v/v) after the separations of A and B isomeric imines from extract P using a neutral alumina-packed column.

Separation of ligand from complex · The chloroform solution of the complex was treated with a suspension of sodium acetate in methanol and 1*M* acetic acid in methanol. The mixture was stirred for 8 hr at room temperature. The mixture was reduced to a small volume *in vacuo* and was extracted with *n*-hexane. The extract was chromatographed on neutral alumina-packed column separating the isomeric imines.

* To whom correspondence should be addressed.

Synthesis of Schiff bases : A mixture of purified amine (0.2 mole) and dl-camphorquinone (0.1 mole) in methanol was refluxed on water-bath for 20 hr. The solvent was removed *in vacuo* at room temperature and the residue was chromatographed on neutral alumina-packed column. Elution with *n*-hexane gave a first fraction of unreacted dl-camphorquinone and second fraction was of a Schiff base with imine group at C(3) position (compound A).

Results and Discussion

The direct reaction of dl-camphorquinone with *n*-butyl amine gave a product (IA) which showed a single band due to $\nu C=O$ and $\nu C=N$. Its ^1H nmr spectra showed three signals of equal intensity at τ 9.22, 9.05 and 8.94 which were assigned to the methyl groups at C(10), C(8) and C(9) respectively. On the basis of analytical data and the Foster's[1] suggestion we tentatively assigned the imine group formation at C(3) position (compound A).

When one mole of nickel chloride was treated with two moles of dl-camphorquinone and four moles of *n*-butyl amine, a single complex (9) was separated, and its chemical analysis suggested that one nickel ion had coordinated, in effect, with one ligand moiety obtained from dl-camphorquinone. The organic compound separated during this reaction was found to contain one imine group in every ligand molecule. However, its ^1H nmr spectra showed three signals of equal intensity at τ 9.17, 9.02 and 8.98 in addition to the signals observed for compound (IA) ; the intensities of these additional signals were about 80 per cent that of the other three signals. These results suggested that when the condensation of α-diketone with *n*-butyl amine was carried out in the presence of nickel(II), both the C(2) and C(3) carbonyl groups participated in the Schiff base formation. We tentatively associated these additional ^1H nmr signals to compound IB containing an imine group at C(2) position. Similarly the $\nu C=O$ observed at the higher frequency was assigned to this compound. We were, however, unsuccessful in separating the proposed isomeric imines IA and IB by the chromatographic techniques or solubility differences

Infrared spectra of the complex (9) showed two bands at 1728 and 1738 cm^{-1} due to $\nu C=O$. Its ^1H nmr spectra displayed the broad signals probably due to the paramagnetic nature of the complex in solution. The complex (9) was therefore a mixture of two ligand-isomeric complexes containing ligands with configurations (A) and (B). These results suggested that the so called steric factors prevalent in the direct condensation reaction were modified in the presence of nickel(II). It will therefore be profitable to study the imine condensation reactions of dl-camphorquinone in the presence of different metal ions to analyse whether it would be possible to separate the isomeric imines. These condensation reactions were carried out in the presence of cobalt(II), nickel(II) and copper(II) chlorides and iodides using *n*-butyl amine, aniline, *o*-toluidine, *m*-toluidine and α-naphthylamine.

On the basis of the elemental analysis, the complexes prepared in the present work were grouped into two classes · Class I, LMX_2 ; Class II, L_2MX_2, L being the Schiff base and X being the halide group (Fig. 1). The complexes of Class I and Class II displayed characteristically different infrared spectra in the region 1755-1630 cm^{-1} (Table 1). Since $\nu C=O$ for Class II complexes was not much shifted from that observed for the free ligand, the carbonyl group in these complexes was not participating in coordination (or metal-oxygen bond was weak). The second carbonyl group was participating in the imine condensation reaction, and it was coordinated to the metal ion. Since $\nu C=O$ in Class I complexes showed a large shift to a lower frequency and a decrease in intensity, it was probably participating in metal-ligand bonding[5]. The intensity of $\nu C=N$ was comparatively high. The Schiff base in these complexes probably behaved as a bidentate ligand, unlike its behaviour as a monodentate ligand in Class II complexes.

The complexes of both the classes were soluble in organic solvents such as benzene and chloroform and they gave non-conducting solutions in nitromethane. The halide groups in these complexes, therefore, participated in metal-ligand bonding, and probably behaved as monodentate ligand (the bridged halide complexes of Schiff bases are generally negligibly soluble in organic solvents). Thus the Class I complexes were four coordinated ; the metal ion in Class II complexes displayed potentially four coordination number.

The nature of metal-ligand bonding in Class I and Class II complexes was further analysed by using the analytical data of the Schiff bases separated from the complexes and of the Schiff bases obtained from *n*-hexane washings of the complexes during synthesis. The Schiff bases obtained from Class II complexes showed three ^1H nmr signals in the region τ 8.70-9.30 of equal intensity. Infrared spectra of these Schiff bases also showed only one band due to $\nu C=O$. These results suggested that only one carbonyl group at one specific position had participated in the imine condensation reaction. We tentatively proposed the presence of an imine group at C(3) position in these compounds.

The Schiff bases separated from the Class I complexes showed two closely spaced $\nu C=O$ group frequencies and a hump was observed on a band associated with $\nu C=N$ (Table 2). ^1H NMR spectra of these ligands showed three additional signals of equal intensity in the high field region corresponding to CH_3 group. These results suggested that the ligand separated from these complexes was a mixture of two isomeric imines. Thus the complexes of Class I were a mixture of isomeric complexes - one isomer containing an imine group

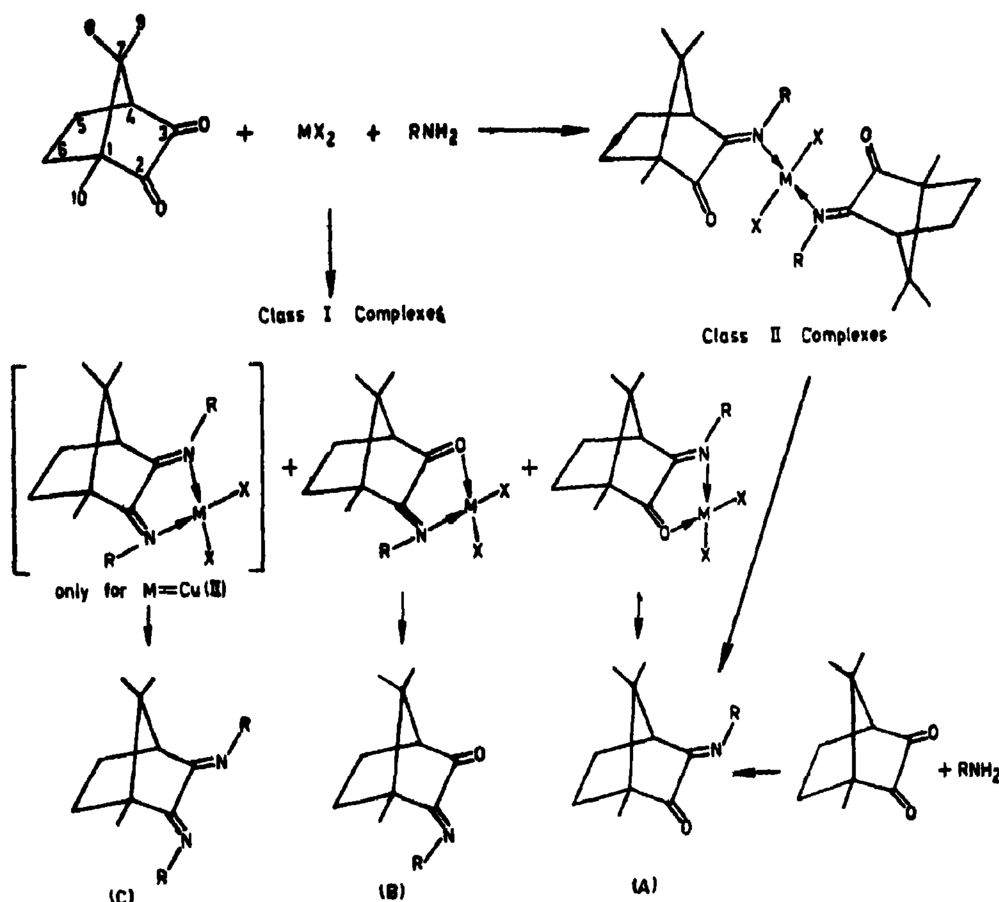


Fig. 1. Reactions of dl-camphorquinone with primary amines. Class I complexes M=Co(II), R=n-butyl, M=Ni(II), R=n-butyl, phenyl, 2-methylphenyl, 3-methylphenyl, M=Cu(II), R=n-butyl, phenyl

Class II Complexes. M=Co(II), R=phenyl, 2-methylphenyl, 3-methylphenyl, α-naphthyl, M=Ni(II), R=α-naphthyl, M=Cu(II), R=2-methylphenyl, 3-methylphenyl, α-naphthyl. $X=Cl^-$ or I^-.

TABLE 1—PHYSICAL DATA OF METAL COMPLEXES

Sl. No.	Complex#	Colour	m.p. °C	IR spectral data $\nu(C=N)/cm^{-1}$	IR spectral data $\nu(C=O)/cm^{-1}$
1.	$(C_{10}H_{14}ONn\text{-}C_4H_9)CoCl_2$	red	93-95	1668(s)	1724(w), 1736(w)
2.	$(C_{10}H_{14}ONC_6H_5)_4CoCl_2C_6H_5NH_2$*	violet	105-107	1653(m)	1748(s)
3.	$(C_{10}H_{14}ONC_6H_5)_2CoI_2$	violet	118-120	1672(m)	1750(s)
4.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)_2CoCl_2$	violet	165-167	1635(m)	1747(s)
5.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)_2CoI_2$	violet	180-182	1664(m)	1744(s)
6.	$(C_{10}H_{14}ONC_{10}H_7)_2CoCl_2$	red	202-204	1652(m)	1750(s)
7.	$(C_{10}H_{14}ONC_{10}H_7)_2CoI_2$	red	246-248	1690(m)	1752(s)
8	$(C_{10}H_{14}ONC_6H_4o\text{-}CH_3)_4CoCl_2C_6H_4o\text{-}CH_3NH_2$**	violet	118-120	1689(m)	1755(s)
9	$(C_{10}H_{14}ONn\text{-}C_4H_9)NiCl_2$	yellowish green	89-90	1650(s)	1728(m), 1738(w)
10.	$(C_{10}H_{14}ONC_6H_5)NiCl_2$	yellow	118-120	1669(s)	1726(m)
10a.	$(C_{10}H_{14}ONC_6H_5)NiCl_2$	yellowish green	128-129	1665(s)	1740(w)
11.	$(C_{10}H_{14}ONC_6H_5)NiI_2$	green	158-159	1658(s)	1720(m), 1738(w)
12.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)NiCl_2$	pale yellow	123-124	1659(s)	1722(w), 1736(w)
13.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)NiI_2$	green	130-132	1661(s)	1723(m), 1735(w)
14.	$(C_{10}H_{14}ONC_{10}H_7)_2NiCl_2$	yellowish green	193-195	1640(m)	1750(s)
15.	$(C_{10}H_{14}ONC_{10}H_7)_2NiI_2$	yellow	228-229	1667(m)	1742(s)
16.	$(C_{10}H_{14}ONC_6H_4o\text{-}CH_3)NiCl_2$	green	136-138	1662(s)	1730(w), 1740(w)
17.	$(C_{10}H_{14}ONn\text{-}C_4H_9)CuCl_2$	green	103-104	1663(s)	1730(m), 1739(w)

(Table 1 Contd.)

18.	$(C_{10}H_{14}ONC_6H_5)CuCl_2$	dark green	138-140	1677(s)	1729(w)
18a.	$(C_{10}H_{14}ONC_6H_5)CuCl_2$	dark green	145-146	1675(s)	1740(w)
19.	$(C_{10}H_{14}ONC_6H_5)CuI_2$	dark green	155-157	1690(s)	1728(w), 1740(w)
20.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)_2CuCl_2$	dark green	132-133	1659(m)	1752(s)
21.	$(C_{10}H_{14}ONC_6H_4m\text{-}CH_3)_2CuI_2$	dark green	145-146	1685(m)	1749(s)
22.	$(C_{10}H_{14}ONC_{10}H_7)_2CuCl_2$	green	155-157	1683(m)	1747(s)
23.	$(C_{10}H_{14}ONC_{10}H_7)_2CuI_2$	dark green	180-182	1664(m)	1748(s)
24.	$(C_{10}H_{14}ONC_6H_4o\text{-}CH_3)_2CuCl_2$	dark green	122-123	1637(m)	1750(s)

All metal complexes gave satisfactory C, H and N analysis

* ν(N−H)/cm^{-1} 3258(m), 3308(m).

** ν(N−H)/cm^{-1} 3238(m), 3287(m).

TABLE 2 – PHYSICAL DATA OF SCHIFF BASES SEPARATED FROM COMPLEXES

Compound No.*	Molecular Formula#	Colour	m.p. °C	Spectral data				
				C(10)†	C(8)†	C(9)†	ν C=N)/cm^{-1}	ν(C=O)/cm^{-1}
IA	$C_{14}H_{23}NO$	yellow	b p 50** 1×10^{-3}mm	9 22	9 05	8 94ᶲ	1666(s)	1744(vs)
IB	$C_{14}H_{23}NO$	orange	b p 50** 1×10^{-3}mm	9.17	9.02	8.98ᶲ	1666(s)	1766(s)
IC	$C_{18}H_{32}N_2$	yellow	59-61	9.19	9 08	8 88	1708(vs) 1662(vs)	—
IIA	$C_{16}H_{19}NO$	dark yellow	116-117	9.12	9 01	8 87	1676(m)	1746(vs)
IIB	$C_{16}H_{19}NO$	pale yellow	122-123	9 10	9.02	8 93	1676(m)	1748(vs)
IIC	$C_{22}H_{24}N_2$	orange	137-139	9.11	9 04	8 82	1708(vs) 1671(vs)	—
IIIA	$C_{17}H_{21}NO$	red	142-143	9.15	9 01	8.90	1663(m)	1759(vs)
IIIA+IIIB	$C_{17}H_{21}NO$	red	141-149	complex multiplets			1674(m) 1654(sh)	1750(s) 1763(m)
IVA	$C_{17}H_{21}NO$	red	137-138	9.13	9 05	8 90	1675(m)	1755(vs)
IVA+IVB	$C_{17}H_{21}NO$	red	139-145	complex multiplets			1678(m) 1674(sh)	1752(vs) 1758(vs)
VA	$C_{20}H_{21}NO$	orange	153 dec	9.21	9 11	8.86	1690(s)	1759(vs)

* IA, 3-N-(n-butyl)dl-camphorquinoneimine, IB, 2-N-(n-butyl)dl-camphorquinoneimine, IC, 2,3-N-(n-butyl)dl-camphorquinonediimine, IIA, 3-N-(phenyl)dl-camphorquinoneimine IIB, 2-N-(phenyl)dl-camphorquinoneimine, IIC, 2,3-N-(phenyl)dl-camphorquinonediimine IIIA, 3-N-(2-methylphenyl)dl-camphorquinoneimine, IIIB, 2-N-(2-methylphenyl)dl-camphorquinoneimine, IVA, 3-N-(3-methylphenyl)dl-camphorquinoneimine, IVB, 2-N-(3-methylphenyl)dl-camphorquinoneimine, VA, 3-N-(1-naphthyl)dl-camphorquinoneimine

All compounds gave satisfactory C, H and N analysis.

† τ Values of CH_3 relative to TMS in $CDCl_3$.

ᶲ Triplet at τ 9 15, 9.11 and 9 07 in the intensity ratio 1 : 2 : 1 for CH_3 of n butyl group

** The exact b p. of imines could not be determined as they decompose even under high vacuum.

at C(3) and a carbonyl group at C(2), and the other isomer containing an imine group at C(2) and a carbonyl group at C(3). These observations prompted us to do a careful separation of the complexes and of the imines separated from the complexes.

The complexes prepared in the present work were found to decompose on both silica and neutral alumina columns, and fractional crystallisation from different organic solvents seemed to be the only method for the separation of the ligand-isomeric complexes. We were successful in separating copper(II) and nickel(II) complexes containing the imines obtained from the condensation of aniline and dl-camphorquinone. One of the two isomeric complexes was more soluble in benzene. Infrared spectra of these isomeric complexes showed a single band associated with νC=O. The ligands separated from these complexes displayed only three characteristic signals due to CH_3 groups (Table 2).

From the *n*-hexane washing of the complexes, it was possible to separate imines on neutral alumina-packed column. The washings of Class II complexes gave only one imine, and its ir and [1]H nmr spectra were identical with those separated from the corresponding complexes. From the *n*-hexane washings of Class I complexes two imines corresponding to formula A and B were separated (Table 2). From the *n*-hexane washings of copper(II) complexes, in addition to the isomeric imines, an appreciable amount of an imine which did not show any band due to νC=O was obtained. It showed two strong bands due to νC=N group, one at 1708 cm^{-1} and the other in the region 1662-1671 cm^{-1}. The new imine contained the imine groups both at C(2) and C(3) positions (formula C). However, a complex containing this ligand was not detected, both from the ir spectra of the complexes and from the spectroscopic properties of the ligands separated from the corresponding complexes.

The crude product of the Schiff base complexes of copper(II) showed a medium to weak intensity band in the region 2136-2146 cm^{-1}. This band disappeared after repeated triturations with diethylether. The presence of this band in the infrared spectra of the crude compound suggested the formation of nitrile[6] from the coordinated ketoimine through the successive steps of the formation of copper(II)-Schiff base complex, oxidation of this complex to copper(III)-Schiff base complex, followed by a two-electron transition forming copper(I)-nitrile complex[7].

The direct condensation reaction of dl-camphorquinone with amine always gave only one imine which was characterised as a compound containing imine group at C(3) position (formula A). In these condensation reactions proper care was taken to avoid the presence of even microamounts of transition metal ions. For example, the condensation reaction of dl-camphorquinone with aniline *containing a trace amount of copper(II)* as an impurity led to the formation of a mixture of isomeric imines. These results suggested that the groups at both C(2) and C(3) should participate in coordination for the formation of isomeric imines.

The role of the metal ion in the formation of isomeric imines seemed to be stereo-electronic. The d-camphorquinone itself displayed an interesting stereochemistry. The observation of isorotation points in the concentration dependent rotatory dispersion curves of d-camphorquinone in *n*-heptane[8] indicated an equilibrium between two stereoisomers. The difference in the polarization of CH_3 groups at 8 and 9 positions by the groups at 2 and 3 positions was indicated from the solvent effect on ^1H nmr spectra of d-camphorquinone and was further confirmed by a large difference ($\Delta\tau = 0.48$) in the ^1H signals of these methyl groups in d-camphorquinoxaline[9]. Such polarisation effects were also displayed by the Schiff bases separated in the present work. The decreasing trend of the difference of the shielding of the two axial methyl groups was as follows

1-naphthylimine>phenylimine>3-methylphenylimine>2-methylphenylimine>*n*-butylimine

The role of the coordinated metal ion was probably to minimise the stereo-electronic differences between the axial methyl groups, and on coordination both the groups at C(2) and C(3) would have more or less similar reactivity. So the complexes in which the groups at C(2) and C(3) were coordinated, (Class I complexes), the imine reaction took place at these groups. A small difference in stereoelectronic factors at C(2) and C(3) was, however, reflected in the relative yields of the two imines as the yield of isomer B was about 80 per cent that of isomer A. A similar stereoelectronic equivalence at the coordinated centres was proposed in the transamination reaction[10,11].

In the imine condensation reaction of dl-camphorquinone with *n*-butyl amine and aniline in presence of copper(II) a compound containing imine groups both at C(2) and C(3) (compoupd C) was separated, while the corresponding copper(II) complex was not separated. However, it seemed that this Schiff base formation reaction proceeded through a transition state consisting of the formation of a α-diimine metal complex, since a direct condensation of dl-camphorquinone and amine did not give a compound containing imine groups both at C(2) and C(3). Similarly, the formation of Schiff base with formula B also proceeded through a complex formation reaction. One might say therefore with caution that these reactions were the homogeneous catalytic reactions.

While preparing this manuscript a work was cited reporting the reaction of d-camphorquinone with 1,3-propanediamine in the presence of nickel nitrate[12]. It was proposed that the complex obtained from this reaction contained an imine group at C(3) position. We are, however, successful in separating compounds containing imine groups at both C(2) and C(3) positions using diamines also ; these results will be reported later.

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Triphenylsiloxy and Diphenylsiladioxy Derivatives of Boron†

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Tris(triphenylsiloxy)borane, phenyl _bis_(triphenylsiloxy)borane, 2-triphenylsiloxy-1,3,2-dioxa-borolanes, -borinanes, -borole and -borin and diphenyl _bis_(1,3,2-dioxa-borolane-2-oxy)silanes have been synthesized by various routes and the reactivity of Si–O–B linkage has been compared with that of Ge–O–B and Sn–O–B linkages. _Tris_(triphenylsiloxy)-borane reacts with acetic acid by cleavage of Si–O bond to give triphenylsilyl acetate and boric acid. 2-Triphenylsiloxy-1,3,2-benzodioxaborole forms 1 : 1 addition complexes with pyridine, triethylamine and aniline. Condensation of diphenylsilane diol with boric acid, _tri_(isopropoxy)borane or phenyldihydroxyborane yields cyclic derivatives.

METALLOSILOXANES, containing a metal-oxygen-silicon linkage, have been explored[1,2] mainly due to two reasons. (a) to attempt the synthesis of siloxane polymers with special properties by incorporating different metal atoms in the siloxane chain and (b) to compare the properties of metal siloxides with metal alkoxides. Trimethylsiloxides of a large number of main group[3] as well as transition metals[4] have been studied. The corresponding triphenylsiloxy derivatives of only a few elements have been described so far and these show considerable thermal and hydrolytic stability in comparison to trimethylsiloxy derivatives[1,2]. The present paper deals with the synthesis and reactions of triphenylsiloxy and diphenylsiladioxy derivatives of boron.

Although there is considerable literature on siloxyboranes[5], the only triphenylsiloxy derivative described so far is $B(OSiPh_3)_3$, obtained by esterification of boric acid with triphenylsilanol[6]. Other monomeric siloxyboranes have been synthesized by various routes which are, in general, extensions of those used for the synthesis of alkoxyboranes. One of us has recently reported the synthesis of various trimethylsiloxyboranes by cleavage reactions of stannoxyboranes with trimethylchlorosilane[7].

Experimental

Triphenylsilanol (B.D.H.) and diphenylsilane diol(Alfa Inorganics) were used as supplied. Tri-(isopropoxy)borane and 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane were prepared by published procedures.

Boron was estimated by Thomas's method. Silicon was estimated as silica. Isopropanol was estimated by oxidation with chromic acid. Molecular weights were determined ebullioscopically in benzene. IR and pmr spectra were recorded on Perkin-Elmer-337 and Perkin-Elmer R12B spectrometers respectively.

Tris(*triphenylsiloxy*)*borane* · A mixture of tri-(isopropoxy)borane (0.54 g; 2.9 mmol) and triphenylsilanol (2.30 g; 8.3 mmol) in benzene (60 ml) was refluxed for about 3 hr and the azeotrope was fractionated (amount of isopropanol in azeotrope: Found, 0.45 g. Calcd. 0.52 g). Excess of solvent was distilled out and the white solid product (2.32 g, m.p. 148°) was finally dried under reduced pressure (Found. B, 1.23; Si, 10.02%; M, 815. Calcd. for $C_{54}H_{45}BO_3Si_3$; B, 1.29; Si, 10.08%; M, 836).

Attempted synthesis of (*isopropoxy*) (*triphenylsiloxy*)*boranes*. (a) A mixture of tri(isopropoxy)-borane (1.74 g; 9.3 mmol) and triphenylsilanol (2.56 g, 9.3 mmol) was refluxed in benzene (40 ml) for about one hour and fractionated (Found: isopropanol 0.53 g. Calcd. 0.56 g). Removal of solvent at 30°/0.01 mm yielded *tris*(triphenylsiloxy) borane (2.55 g, m.p. 148°) (Found B, 1.20; Si, 9.92%).

(b) Reaction between tri(isopropoxy) borane (0.77 g; 4.1 mmol) and triphenylsilanol (2.26 g; 8.2 mmol) in benzene (60 ml) was carried out as in previous experiment yielding isopropanol (Found: 0.42 g. Calcd. 0.49 g) and *tris*(triphenylsiloxy)-borane (2.28 g, m.p. 148°) (Found: B, 1.14; Si, 10.05%).

Phenyl bis(*triphenylsiloxy*)*borane*: Azeotropic removal of water from a mixture of phenyldihydroxyborane (0.56 g, 4.6 mmol) and triphenylsilanol (2.51 g; 9.1 mmol) in benzene (40 ml) followed by drying the product under reduced pressure yielded a white solid (2.92 g, m.p. 134°) (Found: B, 1.55; Si, 8.60%; M, 664. Calcd. for $C_{42}H_{35}BO_2Si_2$; B, 1.70; Si, 8.80%; M, 638).

2-Triphenylsiloxy-4,4,6-trimethyl-1,3,2-dioxaborinane: (a) Refluxing a mixture of 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (1.86 g; 10.0 mmol) and triphenylsilanol (2.76 g; 10.0 mmol) in benzene (60 ml) for one hour, followed by fractionation yielded isopropanol (Found: 0.52 g. Calcd.

† Dedicated to Prof. R. C. Mehrotra, our teacher and guide, on the occasion of his sixtieth birthday.

TABLE 1—SYNTHESIS OF SOME NEW 2-TRIPHENYLSILOXY-1,3,2-DIOXABOROLANES,-BOROLE,-BORIN AND -BORINANES

Sl. No.	Triphenyl silanol (g) (mmol)	G in G(OH)$_2$ (g) (mmol)	Boric acid (g) (mmol)	Product, Molecular formula, Nature	Yield (g) (%)	b.p (°C/mm) m.p. (°C)	Analysis (%) Boron Found (Calcd.)	Analysis (%) Silicon Found (Calcd.)	Mol. wt. Found (Calcd.)
1	2.75 (10.0)	$-CHMeCH_2-$ 0 76 (10 0)	0 61 (9.8)	$C_{21}H_{21}BO_3Si$ Viscous liquid	2 62 (74)	215/1.5	3 18 (3 01)	7.14 (7.80)	385 (360)
2.	2.45 (8.9)	$-CH_2CH_2CH_2-$ 0.68 (8 9)	0 55 (8.9)	$C_{21}H_{21}BO_3Si$ White solid	2.62 (82)	215/1.0 (70)	3 00 (3 01)	7.71 (7.80)	352 (360)
3.	2.23 (8.1)	$-CHMeCH_2CH_2-$ 0 74 (8 3)	0 51 (8 2)	$C_{22}H_{23}BO_3Si$ White solid	2 62 (84)	224/0.5 (60)	2.79 (2.92)	7.37 (7 51)	370 (374)
4.	2.44 (8 8)	$-CMe_2CMe_2-$ 1.07 (9 1)	0.55 (8 9)	$C_{24}H_{27}BO_3Si$ White solid	3.27 (92)	192/0 3 (146)	2 60 (2 69)	6.94 (6.99)	396 (402)
5	2 46 (8.9)	$o-C_6H_4-$ 0.98 (8.9)	0 55 (8 9)	$C_{24}H_{19}BO_3Si$ Viscous liquid	3 51 (100)	—	2 71 (2 75)	7.09 (7.19)	383 (394)
6.	2 57 (9.3)	$o-C_6H_4CH_2-$ 1.16 (9.4)	0 58 (9.4)	$C_{25}H_{21}BO_3Si$ Light yellow solid	3 80 (100)	(101)	2.49 (2.65)	6 37 (6.88)	401 (408)

0.60 g) in the azeotrope. On removing excess of solvent *in vacuo*, the desired product (3.66 g, m.p., 82°; b.p. 217°/0.05 mm) was obtained as a light yellow solid (Found : B, 2.51 ; Si, 6.52% ; M, 368. Calcd. for $C_{24}H_{27}BO_3Si$; B, 2.69 ; Si, 6.99% ; M, 402).

(b) 2,2′-(1,1,3-Trimethyltrimethylenedioxy)*bis*-(4,4,6-trimethyl-1,3,2-dioxaborinane (1.23 g ; 3.3 mmol) was added to *tris*(triphenylsiloxy)borane (2.79 g ; 3.3 mmol) in benzene (20 ml) The mixture was refluxed for 3 hr. Removing the solvent under reduced pressure and subsequent distillation at 217°/0.05 mm yielded 2-triphenylsiloxy-4,4,6-trimethyl-1,3,2-dioxaborinane as a light yellow solid, (3.54 g, m.p 82°) (Found · B, 2.46 ; Si, 6.31%)

(c) Azeotropic removal of water from a mixture of triphenylsilanol (4 51 g, 16.3 mmol) and 2,2′-oxy*bis*(4,4,6-trimethyl-1,3,2-dioxaborinane) (2.20 g ; 8 1 mmol) in benzene (60 ml) gave a light yellowish solid (6 13 g, m p. 82° ; b p 217°/0.05 mm) (Found : B, 2.40 , Si, 6.80%).

2-Triphenylsiloxy-5,5-dimethyl-1,3,2-dioxaborinane · Removal of water azeotropically from a mixture of 2,2′-oxy*bis*(5,5-dimethyl-1,3,2-dioxaborinane) (1.58 g; 6.5 mmol) and triphenylsilanol (3.61 g; 13.1 mmol) gave a clear solution which was further concentrated and kept at room temperature. The product slowly crystallised out as a white solid (3.65 g, m.p. 126°) (Found : B, 2.69 , Si, 7.10% ; M, 375 Calcd. for $C_{23}H_{25}BO_3Si$, B, 2.79 ; Si, 7.24% ; M, 388)

2-Triphenylsiloxy-1,3,2-dioxaborolane Azeotropic removal of water with benzene (60 ml) from a mixture of ethane-1,2-diol (0.59 g ; 9.5 mmol), boric acid (0.59 g ; 9.5 mmol) and triphenylsilanol (2.63 g ; 9.5 mmol) gave a colourless viscous liquid (3.29 g, 100%) (Found : B, 3.01 ; Si, 7.81% ; M, 328. Calcd. for $C_{20}H_{19}BO_3Si$; B, 3.13 ; Si, 8.12% ; M, 346). The product (2.01 g) on distillation under reduced pressure yielded a white solid (0.80 g, b.p. 195°/1.5 mm ; m.p. 81°) (Found · B, 6.57%).

A number of other 2-triphenylsiloxy-1,3,2-dioxaborinanes, -borolanes, -borole and -borin were synthesized by the above procedure. The experimental details are summarised in Table 1.

Amine complexes of 2-triphenylsiloxy-1,3,2-benzodioxaborole · (a) Heat was evolved on adding pyridine (0.20 g ; 2.5 mmol) to a solution of 2-triphenylsiloxy-1,3,2-benzodioxaborole (0 61 g ; 1.6 mmol) in benzene (15 ml). Excess of solvent and pyridine was removed *in vacuo*, leaving a white solid (0 73 g, m.p. 163°) (Found B, 2.14 ; N, 2 45. Calcd. for $C_{29}H_{24}BNO_3Si$; B, 2.29 ; N, 2.96%).

(b) A reddish solid complex (0 54 g, m.p. 144°) was precipitated on adding triethylamine (0.13 g ; 1.3 mmol) to a benzene (5 ml) solution of 2-triphenylsiloxy-1,3,2-benzodioxaborole (0 43 g; 1.1 mmol) (Found B, 2.09 ; N, 2.79 Calcd. for $C_{30}H_{34}BNO_3Si$, B, 2 19 , N, 2 83%).

(c) A white solid complex (1.61 g, m p 189°) was similarly obtained from aniline (0.31 g ; 3.3 mmol) and 2-triphenylsiloxy-1,3,2-benzodioxaborole (1.30 g , 3 3 mmol) in benzene (20 ml) (Found : B, 2.15 ; N, 2 59. Calcd for $C_{30}H_{26}NBO_3Si$; B, 2 22 ; N, 2 8%).

Reaction between tris*(triphenylsiloxy)borane and acetic acid* On adding acetic acid (0.76 g ; 12.7 mmol) to a solution of *tris*(triphenylsiloxy)borane (3.48 g ; 4.2 mmol) in benzene (20 ml) and refluxing the mixture for 3 hr, boric acid (0.21 g, 78%) was precipitated out (Found : B, 16.9. Calcd for H_3BO_3 ; B, 17.5%). The filtrate on removal of solvent gave triphenylacetoxysilane (3 97 g, m.p. 96°) (Found : $OCOCH_3$, 18.16 ; Si, 8.42. Calcd. for $C_{20}H_{18}O_2Si$; $OCOCH_3$, 18.55 , Si, 8.83%)

Reaction between $B(OPr)_3$ and $Ph_2Si(OH)_2$ in 2 3 molar ratio · Tri(isopropoxy)borane (0.68 g ; 3.6 mmol), diphenylsilane diol (1 15 g ; 5.3 mmol) and benzene on being refluxed for 2 hr and then fractionated, yielded, isopropanol (Found · 0.20 g. Calcd. 0 22 g) in the azeotrope and the product (1.15 g, m.p. 212-23°) as a white solid (Found : B, 3.21 ; Si, 12.53. Calcd. for $C_{36}H_{30}B_2O_6Si_3$; B, 3.26 ; Si, 12.68%).

Reaction between boric acid and $Ph_2Si(OH)_2$ in 2 : 3 molar ratio : A mixture of boric acid (0.22 g; 3.6 mmol) and diphenylsilane diol (1.14 g; 5.3 mmol) in benzene (50 ml) was refluxed for 2 hr. Water was removed azeotropically, followed by drying *in vacuo*. A white solid, (1.12 g, m.p. 212-23°) was obtained as the resulting compound (Found: B, 3.17; Si, 12.38. Calcd. for $C_{36}H_{30}B_2O_6Si_3$; B, 3.26; Si 12.68%).

Reaction between $PhB(OH)_2$ and $Ph_2Si(OH)_2$ in 1 : 1 molar ratio : On removal of water from a mixture of phenyldihydroxyborane (0.58 g; 4.8 mmol) and diphenylsilane diol (1.03 g; 4.8 mmol) in benzene (40 ml), followed by drying the product under reduced pressure, a colourless semisolid (1.33 g) was obtained as the final product (Found: B, 3.55; Si, 9.16%; M, 642. Calcd. for $C_{18}H_{15}BO_2Si$; B, 3.58; Si, 9.30%; M,302).

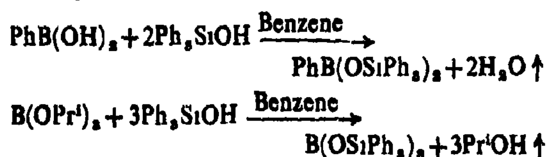
Reaction between $PhB(OH)_2$ and $Ph_2Si(OH)_2$ in 1 : 2 molar ratio : Water was removed azeotropically from a mixture of phenyldihydroxyborane (0.37 g; 3.0 mmol) and diphenylsilane diol (1.30 g; 6.0 mmol) in benzene (60 ml). Removal of excess benzene gave the product (1.50 g) as a colourless semisolid; (Found: B, 2.06; Si, 11.10%; M, 530. Calcd. for $C_{30}H_{25}BO_3Si_2$; B, 2.16; Si, 11.23%; M, 500).

Reactions between boric acid, $Ph_2Si(OH_2)$ and a diol in 2 : 1 : 2 molar ratio : (a) Azeotropic dehydration with benzene (60 ml) of a mixture of boric acid (1.15 g; 18.5 mmol), pinacol (2.20 g; 18.6 mmol) and diphenylsilane diol (2.00 g; 9.3 mmol) yielded a colourless viscous liquid (4.33 g) (Found: B, 4.56; Si, 5.92%, M, 452. Calcd for $C_{24}H_{34}B_2O_6Si$; B, 4.63; Si, 6.00%; M, 468)

(b) Reaction between boric acid (2.00 g; 32.3 mmol), butane-1,3-diol (2.90 g; 32.2 mmol) and diphenylsilane diol (3.48 g; 16.1 mmol) was carried out as in the previous experiment, yielding a colourless viscous liquid (6.57 g) (Found: B, 5.19; Si, 6.75%; M, 401. Calcd. for $C_{20}H_{26}B_2O_6Si$; B, 5.25; Si, 6.82%; M, 412).

Results and Discussion

Phenyl *bis*(triphenylsiloxy)borane and *tris*(triphenylsiloxy)borane have been obtained in quantitative yields by the following routes:



Both these compounds are white crystalline solids, soluble in benzene, carbon tetrachloride and other common organic solvents. The ease of preparation of *tris*(triphenylsiloxy)borane from tri(isopropoxy)-borane may be compared with attempted synthesis of tri(*tert*-butoxy)borane from lower trialkoxy-boranes. The reaction of tri(methoxy)borane and tri(ethoxy)borane with excess *tert*-butanol stops after the removal of 2 moles of methanol and ethanol respectively[8]. The facile nature of silanolysis in comparison to alcoholysis is perhaps due to higher acidity of silanols.

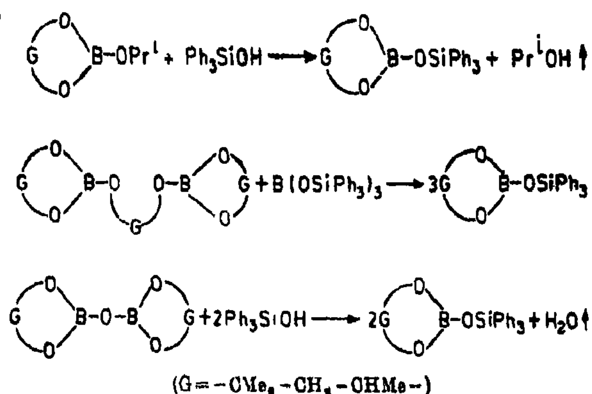
Attempts to synthesize mixed (isopropoxy)-(triphenylsiloxy)boranes, $(Pr^iO)_2(Ph_3SiO)B$ and $(Pr^iO)(Ph_3SiO)_2B$, either by the interaction of tri-(isopropoxy)borane with triphenylsilanol in the appropriate molar ratio or by codisproportionation reaction between $B(OPr^i)_3$ and $B(OSiPh_3)_3$ in refluxing benzene were unsuccessful. Only *tris*-(triphenylsiloxy)borane was obtained as the final product in all these reactions after removing the volatiles under reduced pressure.

The pmr spectra of mixtures of $B(OPr^i)_3$ and $B(OSiPh_3)_3$ in 1 : 2 and 2 : 1 molar ratios in CCl_4 show three sets of isopropoxy methyl doublets in the region 8.6-9.1 τ. The absorption due to aromatic protons occurs as a broad-based peak at 2.2-2.9 τ which is split into three sharp peaks at the apex. This indicates that all the following four species are present in equilibrium:

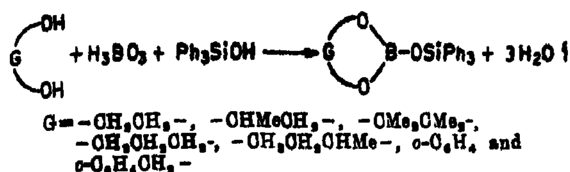


These observations are similar to those for unsymmetrical trialkoxy boranes and are in contrast to the reported isolation[9] of $(Et_3SiO)_2BOMe$, which probably needs rechecking.

In contrast to simple alkoxy siloxyboranes, the unsymmetrical cyclic derivatives show considerable thermal stability and can be readily synthesized by a number of routes. For example, 2-triphenylsiloxy-4,4,6-trimethyl-1,3,2-dioxaborinane, which distils unchanged at 217°/0.05 mm, has been obtained by the following routes



However, the simplest and most convenient route for the synthesis of 2-triphenylsiloxy-1,3,2-dioxaborolanes, -borinanes, -borole and -borin appears to be the azeotropic removal of water from an equimolar mixture of a diol, boric acid and triphenylsilanol in benzene:



G = $-CH_2CH_2-$, $-CHMeCH_2-$, $-CMe_2CMe_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CHMe-$, $o-C_6H_4$ and $o-C_6H_4CH_2-$

All the above compounds are obtained quantitatively in pure state without any trace of $Ph_3SiOGOSiPh_3$ and are generally white solids except the propane-1,2-diol and catechol derivatives which are colourless viscous liquids. All of these are monomeric in refluxing benzene. Like other alkoxyboranes, these compounds are also sensitive towards moisture and hydrolyse to yield the diol, boric acid and triphenylsilanol. Attempts to carry out partial hydrolysis were unsuccessful and it could not be determined whether B–O–Si linkage is initially cleaved or the B–O–C linkage. Most of these triphenylsiloxy derivatives can be distilled unchanged (at ~200°) under reduced pressure (~0.1 mm). Ethane-1,2- and propane-1,3-diol derivatives, however, distil with some decomposition leaving a solid residue which appears to be a mixture of $B(OSiPh_3)_3$ and $(\overline{OG\ O}-B)_2O$.

The characteristic peaks of triphenylsilyl moiety in the ir spectra of triphenylsiloxyboranes are (i) two weak but sharp bands in the 3025-3070 cm^{-1} region due to aromatic C–H stretching modes, (ii) peaks at 1430 cm^{-1} (masked by nujol absorption in solid samples) and 1120 cm^{-1} (the latter being one of the strongest peaks in the spectra) due to silicon-phenyl linkage and (iii) a set of four peaks at 740, 710, 700 and 670 cm^{-1} (the middle peaks being stronger than the outer ones) due to mono-substituted benzene ring. A strong intensity peak due to ν_{as} B–O–Si appears at 1315 cm^{-1} in $B(OSiPh_3)_3$ which is comparable to its position at 1333±8 cm^{-1} in *tris*(trialkylsiloxy)boranes[10]. The ir spectra of 2-triphenylsiloxy-1,3,2-dioxaborolanes and borinanes show ν_{as} B–O–Si at 1300-1350 cm^{-1} and ν_{as} B–O–C at 1350-1450 cm^{-1}, the latter being much stronger than the former.

The pmr spectrum of $B(OSiPh_3)_3$ shows a single broad based (2.3-2.9 τ) peak with an apex at 2.75 τ for the aromatic protons. This broad peak is much better resolved in the spectra of the cyclic derivatives which show two complex multiplets in the region 2.2-2.55 τ (due to two *ortho* protons) and 2.85-2.90 τ (due to *meta* and *para* protons). The strong deshielding effect of silicon on *ortho* protons is probably due to donation of aromatic π electrons to the d-orbitals of silicon. Other peaks due to the alkanedioxy moieties are present at expected positions and the data are summarised in Table 2.

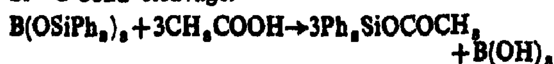
Tris(triphenylsiloxy)borane and 2-triphenylsiloxy-1,3,2-dioxaborolanes and -borinanes do not appear to react with amines. 2-Triphenylsiloxy-1,3,2-benzodioxaborole, on the other hand, reacts exothermally with nitrogen donors (e.g. pyridine, triethylamine and aniline) to form solid adducts of 1 : 1 composition in which coordination occurs from nitrogen to boron.

TABLE 2—RELEVANT PMR AND IR DATA

(G)(O)(O)B–OSiPh₃

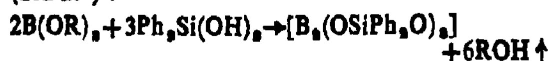
Sl. No	G =	Chemical shift (τ) and shape	Assignment	νB–O–Si (cm^{-1})
1.	$-\overset{a}{C}H_2\overset{a}{C}H_2-$	6.00, s	a	1315
2.	$-\overset{c}{C}H(\overset{a}{C}H_3)\overset{b}{C}H_2-$	8.85, d, J=6 cps 5.40-6.70, m	a b+c	1325
3	$-C(\overset{a}{C}H_3)_2C(\overset{a}{C}H_3)_2-$	8.90, s	a	1315
4.	$-\overset{b}{C}H_2\overset{a}{C}H_2\overset{b}{C}H_2-$	8.25, q, J=5.5 cps 6.10, t	a b	1335
5.	$-\overset{d}{C}H(\overset{a}{C}H_3)\overset{b}{C}H_2\overset{c}{C}H_2-$	8.95, d, J=6 cps 8.20-8.75, m 5.80-6.30, m	a b c+d	1325
6.	$-\overset{b}{C}H_2C(\overset{a}{C}H_3)_2\overset{b}{C}H_2-$	9.22, s 6.54, s	a b	1335
7.	$-C(\overset{a}{C}H_3)_2\overset{c}{C}H_2\overset{d}{C}H(\overset{b}{C}H_3)-$	8.95, overlapping s and d 8.30-8.80, m 5.50-6.20, m	a+b c d	1310
8.	$o-C_6\overset{a}{H}_4$	2.1-3.3, m	a	1325
9.	$o-C_6\overset{b}{H}_4\overset{a}{C}H_2-$	4.9, s 2.0-3.3, m	a b	1300

B–O–Si linkage in triphenylsiloxyboranes appears to be much less reactive than B–O–Ge and B–O–Sn linkages in germanoxy- and stannoxy-boranes[11,12]. Thus, under the same conditions where the latter two linkages are cleaved, the B–O–Si linkage remains unaffected as shown by lack of reaction with acetic anhydride, succinic anhydride and phenyl isocyanate. $B(OSiPh_3)_3$, however, reacts readily with acetic acid in 1 : 3 molar ratio in refluxing benzene yielding boric acid and triphenylsilyl acetate and presumably involving Si–O bond cleavage.



$$B(OSiPh_3)_3 + 3CH_3COOH \rightarrow 3Ph_3SiOCOCH_3 + B(OH)_3$$

Diphenylsiladioxy derivatives: Condensation of tri(isopropoxy)borane or boric acid with diphenylsilane diol in 2 : 3 molar ratio in refluxing benzene yields a white crystalline product which is soluble in benzene and melts in a wide range of temperature (212-23°):

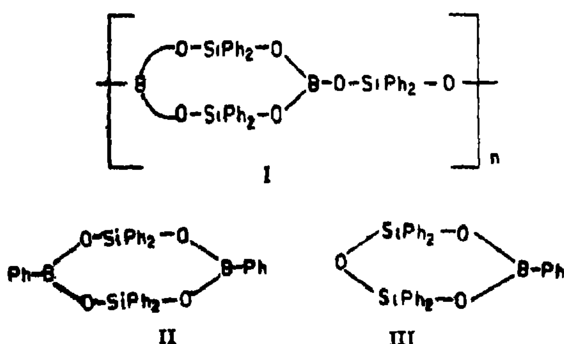


$$2B(OR)_3 + 3Ph_2Si(OH)_2 \rightarrow [B_2(OSiPh_2O)_3] + 6ROH\uparrow$$

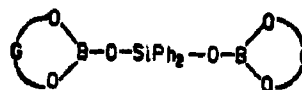
R = H or Pr[i]

Attempts to determine the molecular weight of this compound by ebulliometry were unsuccessful due to the negligible change in the resistance even on taking a sufficiently large amount of the compound. Such behaviour is generally shown by highly polymeric compounds and therefore we believe that the compound is polymeric (Structure I).

Condensation of phenyldihydroxyborane and diphenylsilane diol in 1 : 1 and 1 : 2 molar ratios in refluxing benzene yields cyclic derivatives II and III as viscous semi solids. The pmr spectra of all the three products show only a complex multiplet in the aromatic region (2.0-3.0 τ).



Reaction of diphenylsilane diol with boric acid and a diol (e.g. pinacol or butane-1,3-diol) in 1 : 2 : 2 molar ratio in refluxing benzene yields the corresponding diphenyldi(boroxy)silanes (IV and V) as monomeric viscous liquids which are soluble in common organic solvents and decompose during attempted distillation.



IV, $G = -CMe_2-CMe_2$
V, $G = -CH_2-CH_2-CHMe-$

The ir and pmr spectra of these compounds show close resemblance to those of the corresponding triphenylsiloxy derivatives. For the sake of comparison, it may be mentioned that the corresponding dialkyldi(boroxy)germanes can also be isolated as stable compounds[13]. However, dialkyldi(boroxy)tin derivatives do not appear to be stable and are readily converted into di(boroxy)tetraalkyldistannoxanes[14].

Acknowledgement

One of the authors (P. N. B.) is grateful to C.S.I.R., New Delhi for the award of a Junior Research Fellowship.

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Characterization and Molecular Weight Determinations of Some Organo Poly(aminium phosphate)s—Part V†

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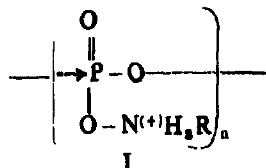
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Paper chromatographic studies and conductance measurements have been used to characterize a few long chain poly(aminium phosphate)s of general composition $(BHPO_3)_n$ (*where BH = organic cations*). Number average molecular weights of these polymers have been determined by titrating *p*H-metrically the poly(phosphoric acids)s obtained by passing the aqueous solution of $(BHPO_3)_n$ derivatives through a column of cation exchange resin. Molecular weight determinations by viscometric data also confirm their long chain polymeric character. The viscosity average molecular weights have been calculated from improved values of intrinsic viscosity, which are determined according to the modified procedure suggested by Nagy, using the linear transformation $G=AF+B$ of usual extrapolation of η_{sp}/C vs C. Here $G=Y/\alpha-x$, $F=x/\alpha-x$ and $\alpha=x_m+x_M$ where $Y=\eta_{sp}/C$ and x_m and x_M denote minimum and maximum concentration.

THE chemistry of inorganic phosphate polymers has been extensively reviewed by several workers[1,2] from time to time. However, systematic investigations in the field of poly(aminium-phosphate)s have not been tried. Only few ammonium[3] and uronium polyphosphates[4,5] of low molecular weights have been prepared and have been used as fertilizers successfully.

Guanidine, an analogue of urea, has been used for the purification of tetraphosphate by recrystallization[6]. Watters *et al*[7] have studied the reaction of guanidine and tetraphosphate anion. Recently, some guanidinium oligophosphates[8] of composition $(H_6CN_3)_nH_{n+2}P_nO_{3n+1}$ (n = 1-10 have been) prepared and have been found to be useful flame retardants for paper and wood.

In the present paper, synthesis of some poly-(aminium-phosphate)s of compositions, ($I_a - I_i$) have been described. The long chain polymeric nature of these derivatives has been elucidated by paper chromatographic analysis[9] and conductance studies[10]. The molecular weights have been determined by end group titration technique[11] and viscosity measurements[12].



where R :

I. a = $-\overset{\overset{S}{\|}}{C}-NHNH_2$ f = $-CO.CH=CH_2$

b = $-(HOOC)CH.(CH_2)_2COOH$ g = $-CH.(CH_3)_2$

c = $-CH_2.CH_2.COOH$ h = $-CO.CH_2.CH_3$

d = $-C_6H_4.OH$ i = $-CS.CH_3$.

e = $-(COOH).CH.CH_2.HOOC$

Experimental

Reagents : All the reagents used were of analytical grade. Extra pure water was used for preparing the solutions. Recrystallized organic compounds were used for the preparation of poly-(aminium phosphate)s.

Synthesis : A technique[13,14] involving the following reaction :



$$\frac{1}{n}(LiPO_3)_n + BHCl \xrightarrow[pH<4]{Acidic} \frac{1}{n}(BHPO_3)_n + LiCl$$

was employed for the preparation of poly(aminium phosphate)s.

Aqueous solutions of poly(lithium phosphate) and organic amine hydrochlorides were mixed in 1 : 1 mole ratio. Monomer formula weight of poly lithium metaphosphate was used. The *p*H of the resulting solution was adjusted below 4. The lowering of the *p*H was considered essential in view of the fact that at this *p*H the lithium ions are loosely associated with the phosphate chain anions. The addition of the organic amine or amide hydrochloride leads to the association of these cations with the phosphate chain anions. Precipitation from the clear solution was carried out by the addition of 2-propanol. The precipitate settled down after cooling for half an hour. It was washed repeatedly with 2-propanol to extract as much water out of it as possible. Lithium chloride, so formed, was also removed by repeated washing with 2-propanol. It was confirmed by the absence of lithium ion in the final product. Finally the product, i.e. the poly(aminium phosphate) was dried under vacuum at room temperature. The composition of these poly(aminium phosphate)s of general formula $(BHPO_3)_n$ was established by analysing them for nitrogen[15] and phosphorus[16]. The results of analysis are recorded in Table 1.

† Part—IV P. C. VYAS, C. K. OZA, R. S. SHARMA and K. C. JAIN, *Polymer Bulletin*, 1980, 2, 221.

TABLE 1—THE NITROGEN AND PHOSPHORUS PERCENTAGE OF VARIOUS ORGANO POLY(AMINIUM PHOSPHATE)S

		P% Calcd. (Found)	N% Calcd. (Found)
Poly(thioaminouronium phosphate) $(CH_6N_2O_3PS)_n$	Ia	18.12 (18.10)	24.56 (24.26)
Poly(1,3-dicarboxy propyl aminium phosphate) $(C_5H_{10}O_7NH)_n$	Ib	13.65 (13.70)	6.16 (6 13)
Poly(1-carboxyethyl aminium phosphate) $(C_3H_8O_5NP)_n$	Ic	18 34 (18.39)	8.28 (8.20)
Poly(m-hydroxyanilinium phosphate) $(C_6H_8O_4NP)_n$	Id	16 40 (16 36)	7.40 (7.36)
Poly(1,2-dicarboxyethyl aminium phosphate) $(C_4H_8O_7NP)_n$	Ie	14 55 (14.50)	6.57 (6.59)
Poly(acrylamidium phosphate) $(C_3H_6O_4NP)_n$	If	20.52 (20.48)	9.27 (9.25)
Poly(isopropyl aminium phosphate) $(C_3H_{10}O_3NP)_n$	Ig	22.27 (22 16)	10.06 (9.96)
Poly(propionamidium phosphate) $(C_3H_8O_4NP)_n$	Ih	20.28 (20.18)	9.14 (9.04)
Poly(thioacetyl aminium phosphate) $(C_2H_6O_3SNP)_n$	Ii	19.97 (19 84)	9 02 (8.96)

Paper chromatographic studies[9] : Whatman chromatographic paper (number 1) was employed for paper chromatographic studies. R_f and R_s values were measured in a New Ebel's[17] solvent by an ascending technique.

Conductance studies : Conductance[10] were measured at different dilutions with the help of a Toshniwal conductivity bridge and a Philips conductivity cell (cell factor 1.49).

Titration of poly(phosphoric acid)s[11] : The number average molecular weights (M_n) of poly(aminium phosphate)s were determined by end-group titration with 0.1*M* sodium hydroxide by using a *p*H meter (systronic type) having a glass and a calomel electrode. The poly(phosphoric acid) solutions used for the titration purpose were obtained by passing the aqueous solution of these poly(aminium phosphate)s through a column of cation exchange resin (Amberlite IR 45-H$^+$ form)[13,14].

Viscosity measurements : The viscosity data were obtained by employing an Ostwald viscometer having an efflux time of 130-180 sec in a thermostatic bath (Toshniwal type), at 30±0.01°. Densities were measured with the help of a pyknometer of 11 ml capacity. All measurements were carried out after 12 hr of dissolution when the solutions attained stability.

Results and Discussion

Paper chromatograms of $(BHPO_3)_n$ derivatives were run in a New Ebel's[17] solvent. This solvent was preferred over other solvents because it gives better separation and fairly large R_f values for cyclic as well as chain phosphates. Well defined spots were observed for all the polymeric derivatives ($I_a - I_i$). Table 2 contains R_f and R_s values for $(BHPO_3)_n$ derivatives. These values fall in the range for those of the poly(lithium phosphate) and

TABLE 2—THE R_f AND R_s VALUES OF VARIOUS POLY(AMINIUM PHOSPHATE)S

Substance	1 run (10 hr) R_f	1 run (10 hr) R_s	2 run (15 hr) R_f	2 run (15 hr) R_s
$NH_4H_2PO_4$	0.79	—	0.80	—
$Na_4P_2O_7$	0.39	0.49	0.41	0 51
$(LiPO_3)_n$	0 02	0.02	0.04	0.05
Ia	0 07	0.09	0.14	0.18
Ib	0.07	0.09	0.13	0.16
Ic	0 06	0.07	0.11	0.14
Id	0.07	0 08	0.12	0.10
Ie	0 07	0.09	0.13	0.17
If	0.06	0.07	0.11	0.14
Ig	0.05	0 06	0.11	0.18
Ih	0.06	0 06	0.11	0.14
Ii	0.07	0.08	0.12	0 15

Graham's salt. A plot (Fig. 1) of R_f values versus negative logarithm of chain length ($-\log n_e$) gives a straight line varying with the degree of polymerization. It is indicative of the fact that the basicity and molar volumes of the organic aminium

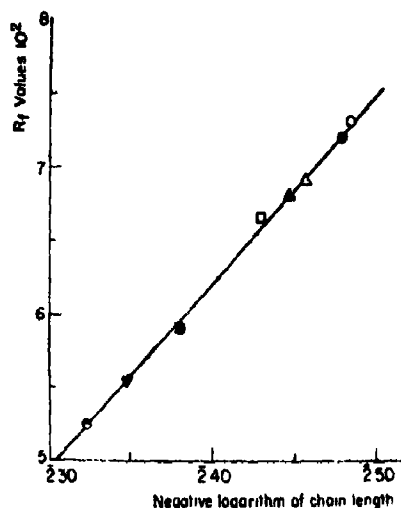


Fig. 1. A plot of R_f values versus negative log of chain length of various poly(aminium phosphate)s.
Ia O-Poly(thioaminouronium phosphate)
Ib. Δ-Poly(1,3-dicarboxy propyl aminium phosphate)
Ic. ■-Poly(1-carboxyethyl aminium phosphate)
Id. ▲-Poly(m-hydroxyanilinium phosphate)
Ie ●-Poly(1,2-dicarboxyethyl aminium phosphate)
If. ▽-Poly(acrylamidium phosphate)
Ig ●-Poly(isopropyl aminium phosphate)
Ih. ▼-Poly(propionamidium phosphate)
Ii. O-Poly(thioacetyl aminium phosphate)

cations play an important role in the precipitation of fractions differing in chain length consisting of $(PO_3)_n$ units in isopropanol-water mixtures. The chromatograms also show two more spots of weak intensity in addition to that for high molecular weight polymeric phosphates. The R_f and R_s values for these spots correspond to those for trimetaphosphate and orthophosphate derivatives. It is due to the initial hydrolysis of polyphosphate chain during dissolution as reported in the case of alkali metal polyphosphates[15]. However, the hydrolysis

of the poly(aminium phosphate) occurs to the extent of 2-4% only during the preparation of the solution[19].

Fig. 2 shows a plot of log of equivalent conductance versus negative log of concentration. It consists of straight lines which run almost parallel to each other. Many poly(electrolytes), Graham's salt and complex polymetaphosphates show similar kind of curves drawn between logarithm of equivalent conductance versus negative logarithm of concentration. This kind of behaviour can be explained on the basis of Fuoss model[20]. Thus, conductance studies are indicative of the poly electrolytic nature of the $(BHPO_3)_n$ derivatives.

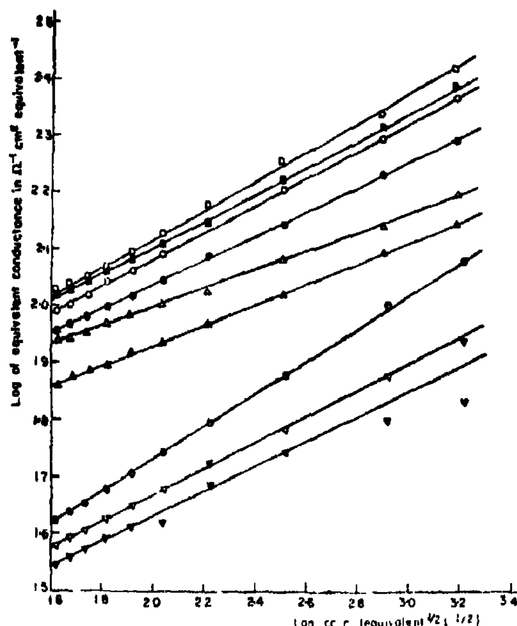


Fig. 2. A plot of log equivalent conductance versus negative log of concentration of various poly(aminium phosphate)s.

Ia=□, Ib=O, Ic=▲,
Id=●, Ie=■, If=⊖,
Ig=▼, Ih=∇, Ii=△,

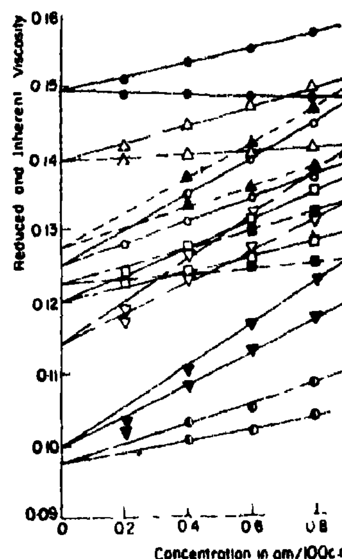


Fig 3 A plot of reduced viscosity and inherent viscosity versus concentration of various poly(aminium phosphate)s.

Ia=■, Ib=▼, Ic=◐,
Id=□, Ie=■, If=▲,
Ig=O, Ih=▲, Ii=□,

The viscosity of $(BHPO_3)_n$ derivatives in 0.035N and 0.07N sodium chloride solution[21] confirms the long chain polymeric character of these derivatives. The reduced (η_{sp}/C) and inherent viscosities ($\ln \eta_r/C$) were plotted against concentration (Fig. 3). Straight lines are obtained which on extrapolation intersect at the same point on Y-axis. This kind of behaviour is characteristic of linear polymers[22] The values for Huggins constant k' and k" were also calculated.

The values for the sum of k'+k" (Table 4) corresponds to 0.5 to 0.6 which are again characteristic of linear chain polymers. The viscosity average molecular weights were determined by using the equation proposed by Strauss[23].

Mehrotra and Gupta[24] have calculated the viscosity average molecular weights of Graham's salt in 0.035N sodium chloride solution instead of sodium bromide and observed that the nature of the swamping electrolyte did not change the reduced viscosity appreciably. The value of K was checked by Gupta[24] in 0.035N sodium chloride solution and it was found to correspond to the same value within experimental errors as given by Strauss *et al*[23]. Hence, the viscosity measurements of poly(aminium phosphate) solutions were carried out in 0.035N sodium chloride solution and viscosity average (M_v) weights were calculated by using the value of K equal to 1.76×10^{-5} and a unit value for that of constant 'a'. The M_v values so obtained are recorded in Table 3.

TABLE 3—THE VALUES OF M_n, η, M_w, $[G_n]$ AND M_w VALUES FOR VARIOUS POLY(AMIMIUM PHOSPHATE)S

Substance	M_n	η	M_w	$[G_n]$	M_w
Ia	2590	0.0995	5655	0 0997	5664
Ib	2760	0.1140	6477	0.1200	6812
Ic	3300	0.1230	6988	0.1250	7102
Id	2815	0.1200	6818	0.1220	6981
Ie	2600	0.0980	5568	0 0990	5667
If	4444	0.1275	7244	0.1300	7389
Ig	3805	0.1495	8495	0.1500	8522
Ih	3692	0.1395	7926	0.1400	7954
Ii	2960	0.1225	6960	0.1250	7102

Nagy *et al*[25] have suggested an improved graphical method for the determination of M_w values for the chain polymers by calculating the intrinsic

viscosity from the viscometric data. The usual straight line relationship between reduced viscosity and concentration is expressed as :

$$Y = ax + b \quad \dots (1)$$

where $Y = \eta_{sp}/C$; x = concentration ; 'a' and 'b' are slope and intercept respectively.

Equation (1) is replaced with the linear transformation

$$G = AF + B \quad \dots (2)$$

where the variables G and F are denoted as :

$$G = Y/\alpha\text{-}x \text{ and } F = \frac{x}{\alpha\text{-}x} \quad \dots (3)$$

and the parameters are $a = A - B$ and $b' = B - \alpha$ .. (4)

In the above equation $Y = \eta_{sp}/C$ and α is the sum of x_m and x_M i.e., the sum of the minimum and maximum independent variable i.e., concentration and A (slope) and B (intercept) are the characteristic constants.

Fig. 4 shows a plot of variable G versus F. The extrapolation of this graph to zero concentration gives the values of parameter B. The values of improved intrinsic viscosity were then calculated from equation (4) with the help of parameter B. The value of α, in equation (4) equal to one has been

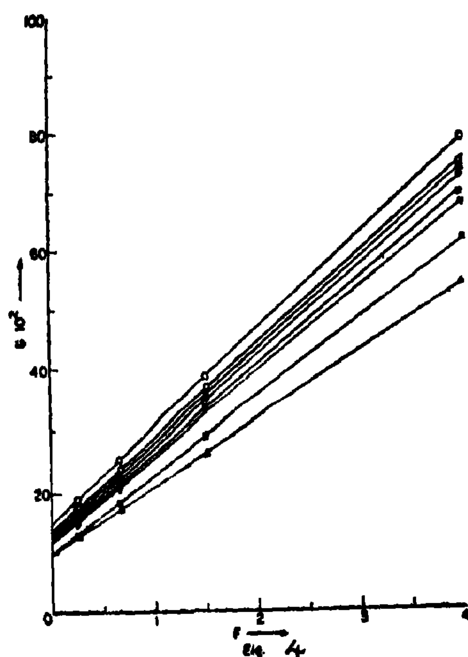


Fig. 4. A plot of variable G versus F of various poly(aminium-phosphate)s.

Ia = ▲, Ib = ∇, Ic = ▼
Id = ⧅, Ie = ■, If = ▲,
Ig = O, Ih = □, Ii = ∇ (same as Ic)

used for these polymer derivatives. So, the value of B directly represents the improved value intrinsic viscosity. But in order to avoid confusion in these two values of intrinsic viscosity, the one obtained by usual plot of η_{sp}/C vs C (Fig. 3) is represented by [η] and the one obtained by equation (4) is represented by [Gn]. Both these values are recorded in Table 3. It is revealed from the table that both these values differ by 2-4%. However, the suggested method ensures an uniform error distribution in the measurement of viscosity data which deviates from the straight line relationship in usual graphical method of η_{sp}/C vs C at higher dilutions. Hence, the improved values of intrinsic viscosity [Gn] can be used for calculating the more reliable viscosity average molecular weights according to the equation (5).

$$(x_M + x_m)[Gn]_{c \to 0} = 1.76 \times 10^{-8} M_w^* \quad (5)$$

The M_w^* values so obtained are recorded in Table 3.

The viscosity of $(BHPO_3)_n$ derivatives were also determined in 0.07*N* sodium chloride solution[21]. The values for intrinsic viscosity in 0.07*N* and 0.035*N* sodium chloride solution are recorded in Table 4. From the table it is observed that the

TABLE 4—INTRINSIC VISCOSITY VALUES IN 0.035*N* AND 0.07*N* SODIUM CHLORIDE AND AV. $k'+k''$ FOR POLY(AMINIUM PHOSPHATE)S

	[η] in 0.035*N* NaCl	[η] in 0.07*N* NaCl	av. $k'+k''$
Ia	0.0995	—	0.65
Ib	0.1140	0.0095	0.56
Ic	0.1230	—	0.62
Id	0.1200	0.1080	0.57
Ie	0.0980	—	0.61
If	0.1275	0 1100	0.55
Ig	0.1495	0.1380	0.51
Ih	0.1395	0.1275	0.53
Ii	0.1225	—	0.54

intrinsic viscosity [η] is decreased in 0.07*N* sodium chloride which suggests that increase in concentration of swamping electrolyte affects the draining behaviour of these polymers.

The number average molecular weights (M_n) determined from end-group titration were found to be in the range 3000-4000. The ratio of M_w/M_n corresponds to about 2.1 to 2.3 which is indicative of most probable distribution of molecular weight in the case of these poly(aminium phosphate)s. Van-Wazer[26] has suggested a Poisson distribution in case of middle group of the $(PO_3^-)_n$ chain in case of alkali metal phosphates i.e., the viscosity average molecular weight is nearly equal to the number average molecular weight.

The conclusion rests on an approach used by Flory[27] in considering the random reorganization in linear organic polymers. It was assumed that terminal phosphate groups of the P–O–P chain are not involved in the reorganization process. Ohashi

et al[21] determined the viscosities of sodium phosphates and Graham's salt. It has been stated that distribution of molecular weights is not exactly the Poisson distribution for lower molecular weight (lower than 10300) samples. In general for a polydisperse polymer

$$M_w > M_v > M_n$$

with differences increasing as the molecular weight distribution broadens. The ratio M_w/M_n can be taken as a measure of distribution of molecular weight in a polymer sample. This ratio is approximately two for polymers having a 'most probable distribution' as expected in case of step reaction (condensation) polymerization[28]. As poly(aminium phosphate)s have been isolated by reacting poly(lithium phosphate)s having weight average molecular weights in the range 8000-10000, the ratio of M_w/M_n for these polymers is more than two also. Therefore, it can be predicted that molecular weight distribution for poly(aminium phosphate) is not exactly Poisson and corresponds to a 'most probable distribution' as expected in case of linear chain polymers.

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A New Approach to Astatistical Stabilisation of Cu(II) Ternary Complexes Containing Tertiary Amines and O—O⁻ Co-ordinating Ligands

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The formation constants of the complexes of the type [CuAL], where A = 2,2′-dipyridyl, 1,10-phenanthroline, 2-(2′-pyridyl)benzimidazole or 2-(2′-pyridyl)imidazoline and L = acetylacetone or benzylacetone have been determined in dioxan-water (1 : 1 v/v) solutions and $\mu = 0.2$ ($NaClO_4$) at 30°. The formation constant values have been determined by graphical method and further refined by using a computer programme. The value of Δlog K (log K^{MA}_{MAL} − log K^{M}_{ML}) is found to be positive in [CuAL] complexes. The fact that Δlog K is positive in Cu(II) complexes, can be explained to be due to repulsion between metal dπ electrons and electron density over L. The study of uv and visible spectra also confirm this concept.

THE name organic is synonymous with life and hence the term "bio inorganic" appears self contradictory. But it has been recently realised that the metal ions have an important role to play in biochemical reactions. Inorganic chemists have thus been encouraged to synthesise model compounds which closely mimic the naturally occuring compounds. Through the study of the properties of these synthetic models, they try to evolve principles governing the biochemical processes.

Study of the mixed-ligand complexes[1-3] is gaining importance because it provides models for the metalloenzyme reactions. The mixed-ligand complexes, involving aromatic tertiary amines, are being studied in detail because of the similarity of the aromatic tertiary amines with imidazole which occurs commonly in metalloenzymes.

Ternary complex formation is statistically favoured. There is further astatistical[2,3] stabilisation due to various reasons. In the complexes [MAL], where A is a tertiary diamine like dipyridyl, it has been observed that the mixed-ligand formation constant K^{MA}_{MAL} is higher than expected from statistical considerations[4]. This has been explained to be due to M→ dipy π interaction[5,6]. As a result, the electron density over the metal ion is reduced and the effective electronegativity of $[MA]^{2+}$ is almost the same as $[M(H_2O)_6]^{2+}$. Thus, the σ bonding tendency of L to combine with $[CuA]^{2+}$ is not significantly reduced. As M→A π interaction goes on increasing the ternary complex is stabilised more[7].

[MA] complexes are known to have discriminating effect towards secondary ligand (L) with co-ordinating atoms, N−N, N−O⁻ and O⁻−O⁻ [8]. The stabilisation of ternary complexes [MAL] is in the order O⁻−O⁻ > O⁻−N > N−N. In [CuAL] complexes the stabilisation is greater and Δlog K (log K^{Cu}_{CuAL} − log K^{Cu}_{CuL}) is positive, in cases where L co-ordinates through two O⁻. This extra stabilisation was explained by Sigel[9] to be due to interligand π interaction between A and L through the metal dπ orbital where L is catechol. However, a positive Δlog K is observed even when L is purely σ bonding ligand like malonate ion[10,11]. In order to explain such cases an alternate explanation was extended by us in terms of electron repulsion[11-13]. In the formation of binary complexes, there is electron repulsion between the metal dπ electrons and the lone pair of electrons (if any) present on the σ bonding ligand L. However, in ternary complexes, due to back donation of electron through π bonding from the metal ion to A molecule, the electron density on $[CuA]^{2+}$ is reduced. Therefore, the repulsion between the metal dπ electrons and the additional lone pair of electrons over the secondary ligand (L) is less in the ternary complexes. There is no extra lone pair of electrons present on σ bonding N atom and hence this effect is not felt in N - N co-ordinating ligands. In ligand coordinating through N−O⁻ there is lone pair of electrons over the carboxylate O⁻. Due to the decrease of the electron repulsion in the ternary complexes, Δlog K is much less negative in N−O⁻ than in N−N co-ordinating ligands. In case of malonate, there are lone pair of electrons over both carboxylate anions and hence the effect is more pronounced leading to positive Δlog K in [CuAL].

Even in cases of complexes [CuAL], where L = anions of catechol, dihydroxynaphthalene or its derivatives[14], salicylaldehyde, 2-hydroxy-naphthaldehyde or its derivative[15], it has been shown by uv spectral studies that though there is π interaction in $[CuA_2]$ and $[CuL_2]$ complexes, there is one to one correspondence between the uv spectral bands of the mixed-ligand complex [CuAL] with that of [CuA] and [CuL], with no significant change in band positions. This shows that there is no interligand π interaction between A and L through the metal dπ orbitals, as suggested by

Sigel[9]. Hence, in these complexes also the greater stabilisation and positive $\Delta\log K$ can be explained[11-13] in terms of the lowering of the repulsion between metal $d\pi$ electrons and the ligand lone pair electrons in the ternary complex.

In the case of [CuAL], where L is 2,3-dihydroxynaphthalene, $\Delta\log K$ is less positive than in the case of catechol, because the electron density due to the extra lone pair of electrons over two O^- is delocalised over two rings. Thus, the repulsion effect is less in the binary complex and lowering of repulsion is also less in the ternary complex leading to a less positive $\Delta\log K$ value. In the case of 1,8-dihydroxynaphthalene with the two O^- on the two different benzene rings, the stabilization of the ternary complex is still less and $\Delta\log K$ is negative, though the coordination of L is from two O^-.

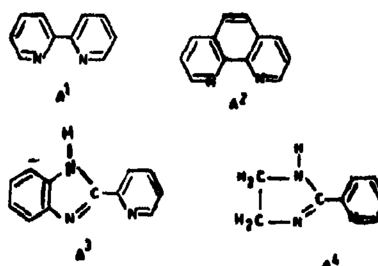
It had been observed by Sigel[16] earlier that electron-withdrawing substituents over L lower the stability of the ternary complex, whereas electron-donating groups increase the stability. He could not, however, extend any explanation in terms of the concept of interligand π interaction. It was observed by us in [Cu-A-tiron], [Cu-A-protocatechate] and [Cu-A-pyrogallol] complexes[14] that $\Delta\log K$ values are less positive than in the case of [Cu-A-catecholate]. This can be explained in terms of our concept of lowering of electron repulsion in the ternary complex. The substituted sulphonate, carboxylate or the hydroxy group withdraws electron density from the ring. Thus, the negative charge over O^- is less in these cases than in the unsubstituted catecholate and hence $\Delta\log K$ is less positive.

In ternary complexes, [CuAL], where L=dopamine or adrenaline also $\Delta\log K$ is less positive or negative. This is because the amino group does not take part in coordination. This remains protonated in the range of coordination of the ligand. This protonated amino group withdraws electrons from the catecholate ring and hence the ternary complexes are not stabilised to the same extent as in the case of [Cu-A-catecholate].

The study of [Cu-A-catecholate] type of complexes is interesting because they provide a model for metalloenzyme reactions. The effect of substituted group, not directly coordinating to the metal ion, on the ternary complex stability also throws light on the role of the substituents on the carrier ligand, not directly involved in coordination with metal ion, on the stability of the metalloenzyme substrate complex.

β-Diketone complexes are known to have pseudo aromatic character due to π interaction between the metal $d\pi$ electrons and $p\pi$ electrons delocalised over the diketonate ion[17]. In [Cu(dipy)(acac)], $\Delta\log K$ was found to be nearly zero indicating greater stabilization of the ternary complex[18]. However, in case of the ternary complexes [CuAL], where L=β-ketoanilide, $\Delta\log K$ is positive[18]. Thus, though Cu→β-ketoanilide π interaction is less, the ternary complexes involving β-ketoanilide are more stable. This has been explained to be due to the presence of an additional lone pair of electron over the anilide nitrogen which increases the electron density in the β-ketoanilide chelate ring leading to positive $\Delta\log K$. Similar effect and positive $\Delta\log K$ is observed in ternary complexes of the type [CuAL], where L=salicylanilide derivatives[18]. By the substitution of an electron withdrawing bromine group over the secondary ligand, $\Delta\log K$ is found to be less positive.

In the present work, study of the complexes [CuAL], where A=2,2'-dipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2'-pyridyl)benzimidazole (A^3) or 2-(2'-pyridyl)-imidazoline (A^4) and L=acetylacetone (L^1) or benzylacetone (L^2) have been carried out. The structures of ligands A are shown in Fig. 1.



Experimental

All the reagents used were of A.R. grade except 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline which were prepared by known method[19]. TLC and melting points indicate purity of the compounds. Analysis agrees with expected percentage of C, H and N.

The proton-ligand and metal-ligand formation constants were determined in dioxan-water (1 : 1 v/v) solution and μ=0.2 ($NaClO_4$) at 30°.

The values of $\bar{n}_H$, K_1^H, $\bar{n}$, pL, $\log K_1$ and $\log K_2$ were calculated by carrying out normal Irving-Rossotti titration[20,21]. The titrations were carried out under an atmosphere of nitrogen in thermostatic bath with temperature 30±1°. The formation constants of ternary complexes were determined by an extension of Irving-Rossotti technique[6]. Expanded scale pH meter, pH 821 of Elico make, with an accuracy of ±0.01 pH units was used. At $\bar{n}=0.5$ in the formation curve, $pL=\log K^{MA}_{MAL}$. More precise values were obtained by plotting pL against $\log 1-\bar{n}/\bar{n}$ and obtaining a straight line, wherein $\log K^{MA}_{MAL}=pL-\log 1-\bar{n}/\bar{n}$. The average values have been recorded in Table 2. In each individual measurement, pH values were corrected for dioxan-water (1 : 1 v/v) medium using the method suggested by Van Uitert and Hass[22].

All the formation constants were subjected to refinement by using the computer programme

SCOGS[22]. The refined values of proton-ligand and binary metal-ligand formation constants were first obtained. These refined values were used for the refinement of the ternary complex formation constants in two ways:

(i) by considering the species present in the solution to be LH, L, [CuA] and [CuAL]

and (ii) taking into account all possible species to be present in solution i.e., LH, L, AH_2, A, [CuL], $[CuL_2]$, [CuA], $[CuA_2]$ and [CuAL].

The refined values obtained by the computer technique, have been presented in Tables 1 and 2. In cases of $[CuA^3L]$ and $[CuA^4L]$, calculation of mixed-ligand formation constants considering all possible species could not be done. This is because formation of $[CuA^3]$ and $[CuA^4]$ is complete at very low pH and hence the formation constant of $[CuA^3]$ and $[CuA^4]$ could not be determined by pH metric titration. The formation constants were, therefore, determined by presuming complete formation of [CuA].

TABLE 1—PROTON-LIGAND AND BINARY COMPLEX STABILITY CONSTANTS OF Cu(II) IN DIOXAN-WATER (1 : 1 v/v) AND μ=0.2 ($NaClO_4$) AT 30°

Ligand	K_1^H	$\log K_{CuL}^{Cu}$	$\log K_{CuL_2}^{CuL}$
L^1	9.48	9.45	7.81
L^2	9.56	9.38	7.84

TABLE 2—STABILITY CONSTANTS OF TERNARY COMPLEXES OF Cu(II) IN DIOXAN-WATER (1 : 1 v/v) AND μ=0.2 ($NaClO_4$) AT 30°

	$\log K_{CuAL}^{Cu}$											
	A^1			A^2			A^3			A^4		
	I	II	Δlog K	I	II	Δlog K	I	II	Δlog K	I	II	Δlog K
L^1	9.70	9.56	+0.11	9.70	9.56	+0.11	10.00	10.12	+0.56	9.00	9.13	−0.32
L^2	9.90	10.21	+0.33	9.88	9.98	+0.15	10.60	10.63	+0.30	9.40	9.50	−0.33

I—An extension of Irving-Rossotti titration technique.
II—Computer method.

TABLE 3—ELECTRONIC SPECTRAL BAND ENERGIES (nm) AND log ε OF FREE LIGANDS, BINARY COMPLEXES AND MIXED-LIGAND COMPLEXES IN DIOXAN-WATER (1 : 1 v/v) MEDIUM

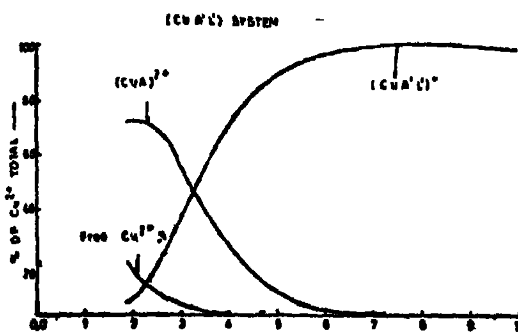
Compound	nm (log ε)
A^1	236.9(4.15), 289.1(4.18)
$[CuA^1_2]^{2+}$	240.3(4.6), 301.2(4.56), 312.5(4.51), 714.3(2.79)
L^1	279.3(4.08)
L^2	250(3.87), 316.4(3.50)
$[CuL^1_2]$	288.1(3.98), 384.6(2.44), 666.6
$[CuL^2_2]$	251.2(3.76), 322.5(3.90), 387.5(2.41), 322.5
$[CuA^1L^1]^+$	243.9(4.04), 289.0(4.07), 295.8(4.14), 312.5(3.95), 387.5(2.58), 625(1.89)
$[CuA^1L^2]^+$	251.2(4.29), 301.2(4.26), 312.5(4.24), 335.5(3.90), 384.6(2.47), 621.1(1.75)

Spectral measurement: The spectra were recorded on a Carl Zeiss Specord UV visible spectrophotometer with 1 cm quartz cells using dioxan-water (1 : 1 v/v) as solvents. Solutions of concentration 10^{-4} to 10^{-2} mol dm^{-3} were used for uv and visible regions, respectively. Spectra of free ligand, $[CuA_2]$, $[CuL_2]$ and [CuAL], prepared by direct mixing of Cu(II) and ligands in required proportions, were obtained.

Results and Discussion

It is interesting to observe that in the case of the ternary complex $[CuAL]^+$, the values of the formation constants obtained by the use of the extension of Irving–Rossotti titration technique, presuming the formation of complex in two distinct separate steps, Cu+A⇌[CuA] and [CuA]+L⇌[CuAL], and the values obtained by using the computer technique are nearly equal in all the cases. This shows that the presumption, that $[CuA]^{2+}$ formation is almost complete in the lower pH range and L^- combines with $[CuA]^{2+}$ in forming $[CuAL]^+$, is valid. This is further confirmed by observing the plot of the concentration of various species (as percentage of total Cu^{2+} present) against pH as shown in Fig. 2. It is observed that in the lower pH range Cu^{2+} and $[CuA]^{2+}$ are major species and in the higher pH range the major species are $[CuA]^{2+}$ and $[CuAL]^+$ totalling to almost 100%. The concentration of other species are negligible.

It is observed that Δlog K is positive except when $A = A^4$. The value of mixed-ligand formation



2. Variation of concentration of different species with pH.

constants depends on Cu→A π interaction and the order is found to be as follows :



$$[CuA^3L] > [CuA^1L] \approx [CuA^2L] > [CuA^4L]$$

It shows that Cu→A π interaction in $[CuA^1]$ and $[CuA^2]$ are of equal extent. However, in $[CuA^3]$ the co-ordination is from one pyridine N and one benzimidazole ring N and hence Cu→A π interaction is greater. This results in an increase in the formation constants of ternary complexes and $\Delta\log K$ becomes more positive. In the cases of $[CuA^4L]$, $\Delta\log K$ is found to be negative because there is co-ordination from one pyridine N and one imidazoline ring N. π interaction is possible only with pyridine ring as imidazoline ring is saturated and has no delocalized π electron cloud. Thus, it is less π interacting than the other primary ligands A^1, A^2 and A^3.

In order to explain the positive $\Delta\log K$ value in [CuAL] complexes, Sigel and coworkers[9] considered interligand π interaction between A and L. A similar explanation could be extended for the present [CuAL] complexes. However, an observation of the uv spectra of the complexes does not support interligand π interaction.

UV spectra · The specific bands are discussed in the ternary complexes, $[CuA^1L_1]^+$. Dipyridyl (A^1) shows bands at 236.9 and 289.1 nm The band in the lower energy region corresponds to $\pi\rightarrow\pi^*$ transition. On co-ordination with metal ion $[CuA^1_2]^{2+}$ shows bands at 243.9, 301.2 and 312.5 nm. The appearance of a new band and shift in $\pi\rightarrow\pi^*$ transition shows that there is interaction between π orbitals of Cu(II) and those of dipyridyl molecule. The band in acetylacetone (L^1) is observed at 279.3 nm. In the case of $[CuL^1_2]$, bands are observed at 288.1 nm and 384.6 nm. The band at 384.6 nm corresponds to $n\rightarrow\pi^*$ transition. This indicates that there is ligand to metal charge transfer interaction.

In the ternary complex $[CuA^1L^1]^+$ there is almost one to one correspondance of bands with that in $[CuA_2]^{2+}$ and $[CuL_2]$, with no significant change in their positions. Thus, although there is metal-ligand π interaction in the binary complexes, there is no significant change in the π orbital energies due to mixed-ligand complex formation. This indicates that in these complexes also there is no significant interligand π interaction through metal $d\pi$ orbitals. The spectra of other [CuAL] complexes revealed the same fact.

An alternative explanation has, therefore, to be extended for positive $\Delta\log K$ values in these complexes. The greater stability of the ternary complexes can be explained in terms of release of electron-repulsion. In the formation of the binary complex, there is electron-repulsion between the metal ion $d\pi$ electrons and lone pairs of electrons present over the O^- of ligand L. This repulsion lowers down the formation constant of [CuL] complexes. However, in the ternary complexes, there is back donation of metal $d\pi$ electrons to the primary ligand through π bonding and hence the electron density on the metal ion is reduced in $[CuA]^{2+}$, resulting in lowering of repulsion between metal $d\pi$ electrons and the ligand lone pair of electrons. Hence, the tendency of L to combine with $[CuA]^{2+}$ is more than the tendency to combine with Cu^{2+}, and $\log K^{CuA}_{CuAL}$ is greater than $\log K^{Cu}_{CuL}$ resulting in positive $\Delta\log K$ in ternary complexes [A-Cu-acetylacetone] and [A-Cu-benzylacetone].

Visible spectra The study of ligand field spectrum is also interesting. It is normally expected that in mixed-ligand complex [MAL], the ligand field splitting is average of that in the two binary complexes $[MA_2]$ and $[ML_2]$. However, in the complexes of the present study $[CuA^1L^1]^+$, where L co-ordinate through $O-O^-$, the d-d transition band is at higher energy than in $[CuL^1_2]$ or $[CuA^1_2]^{2+}$. This is because Cu→dipy π interaction stabilises L→Cu σ interaction (where L co-ordinates through $O-O^-$) due to lowering in electron-repulsion between metal $d\pi$ electrons and the lone pair of electrons over O^-. Conversely, L→M σ interaction increases M→dipy π interaction. Thus, the two ligands mutually stabilise each other. Consequently, ligands A and L create stronger field in [CuAL] than in $[CuA_2]$ or $[CuL_2]$. The positive shift in the d-d band position of $[CuAL]^+$ complex from the average of $[CuA_2]$ and $[CuL_2]$ can be considered as the extent of stabilisation of the ternary complex.

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Relationships Between the Direction of Shifts in the Carbon-oxygen Stretching Frequencies of Carboxylato Complexes and the Type of Carboxylate Coordination

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On the basis of the directions of the shifts in the ir frequencies of ν_{asym} OCO and ν_{sym} OCO from those for ionic carboxylate, the various modes of carboxylate binding —unidentate, chelating bidentate (unsymmetrical and symmetrical) and bridging bidentate (unsymmetrical and symmetrical)—are distinguished. This criterion is superior to the previously better-known ir spectral criterion because of its uniform applicability and its capability of making even finer distinctions between symmetrical and unsymmetrical types within the chelating and bridging bidentate modes. This finding is based on the analysis of ir spectral data of a very large number of acetato— and trifluoroacetato compounds with known crystal structures.

ACETATE ion can coordinate a metal ion in a variety of ways; as a simple unidentate ligand, as a chelating bidentate group (unsymmetrical or symmetrical) and as a bridging bidentate group (unsymmetrical or symmetrical). Acetate ion is of such a low symmetry (C_{2v}) that all the fifteen vibrational modes are ir active even in the free ion and further lowering of symmetry upon coordination is not expected to increase the number of ir bands due to acetate group. However, of the fifteen fundamental vibrational modes for the acetate the modes due to COO^- part namely antisymmetric OCO stretch (ν_{asym} OCO), symmetric OCO stretch (ν_{sym} OCO) and OCO bend are expected to be more sensitive to coordination and the frequencies due to them could be shifted on complexation. The shifts in the first two have indeed been observed and the magnitude of separation (Δ) between the frequencies due to ν_{asym} OCO and ν_{sym} OCO in different compounds has been found to be affected by several factors[1-8]. Curtis[4], Grigor'ev[5], Deacon[6], Deacon and Phillips[7] and Alcock *et al*[8] made more systematic studies of the relationship between the magnitude of Δ and the mode of coordination of the acetate group and thus developed the Δ criterion for distinguishing the main types of acetate binding – unidentate, chelating bidentate and bridging bidentate. Their conclusions, though not in complete agreement with each other, may be broadly summarized as: the compounds which have unidentate acetate groups have Δ values of the very high order while those with chelating and/or bridging bidentate type have Δ values significantly less than the value in ionic acetate.

As has been recently demonstrated[9,10], the Δ criterion, though helpful in identifying some modes of acetate coordination, is incapable of distinguishing all the main types of acetate binding. Moreover, the Δ value may frequently be similar for two different types or different for two similar types of coordination (see Table 1). In view of the absence of a clear-cut differentiation on this basis it is not a good criterion. Its earlier success and apparent validity[4-8] were based mainly on the fact that it was developed from the analysis of, and subsequently tested on, a very few cases of known molecular structure[10]. It has no theoretical sanction either to enforce its use in the face of its gross limitation; although originally it appeared to have a basis in the fundamentals of bonding[1-8] ultimately it proved to be largely empirical[10].

We have examined the ir spectral data of 46 acetato- and trifluoroacetato complexes whose crystal structures had been determined by various earlier workers. From the analysis of the values of ν_{asym} OCO and ν_{sym} OCO in these compounds it has been observed that in compounds with unidentate carboxylate groups the directions of the shifts in the frequencies due to ν_{asym} OCO and ν_{sym} OCO are higher and lower respectively relative to those for ionic carboxylate. Unidentate coordination removes the equivalence of two oxygen atoms and two C–O bond orders are appreciably affected giving a pseudo ester type configuration. In the case of chelating and bridging bidentate carboxylates there is little change in the C–O bond orders and the movement of frequencies is less in comparison to those for the unidentate coordination; here the directions of the shifts in the positions of ν_{asym} OCO and ν_{sym} OCO relative to those in ionic carboxylates are as unsymmetrical bridging bidentate: higher, almost the same; symmetrical bridging bidentate: higher, higher; unsymmetrical chelating bidentate: almost the same, higher; and symmetrical chelating bidentate: lower, higher.

This set of relationships between the modes of carboxylate binding and the directions of the shifts in the frequencies of ν_{asym}OCO and ν_{sym}OCO may be used as an ir spectral criterion for the mode of carboxylate binding. This criterion, based on the

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TABLE 1—INFRARED AND STRUCTURAL DATA FOR ACETATO AND TRIFLUOROACETATO COMPOUNDS

Sl. No.	Compound	$\nu_{asym}OCO$	$\nu_{sym}OCO$	Δ(IR)Ref.	Directions of the shift in comparison to those in ionic carboxylates $\nu_{asym}OCO$	$\nu_{sym}OCO$	Mode of binding	Ref. (Cryst. Struct.)
1.	$Co(NH_3)_5OCOCH_3.(ClO_4)_2$	1603	1380	223(11)	Higher	Lower	Unidentate	(48)
2.	$Ni(teta)(OCOCH_3)_2$[a]	1583	1405	178(4)	Higher	Lower	Unidentate	(4)
3.	$Hg(OCOCH_3)_2$	1600	1368	232(12)	Higher	Lower	Unidentate	(49)
4.	$PhHg(OCOCH_3)$	1615[d] 1590	1379[d] 1368	232(13)	Higher	Lower	Unidentate	(50)
5.	$[Me_2CO(O)_2]CHHg(OCOCH_3)$	1618[d] 1580	1309	290(14)	Higher	Lower	Unidentate	(51)
6.	$Na[H(OCOCH_3)_2]$	1710	1410	310(15)	Higher	Lower	Unidentate	(15)
7.	$Ph_4Sb(OCOCH_3)$	1633	1320	313(16)	Higher	Lower	Unidentate	(52)
8.	$(Cyclo\text{-}C_6H_{11})Sn(OCOCH_3)$	1645	—[e]	—[e](17)	Higher	—	Unidentate	(17)
9	$K[H(OCOCF_3)_2]$	1792	1420	372(18)	Higher	Lower	Unidentate	(53)
10.	$Cs[H(OCOCF_3)_2]$	1790	1408	382(18)	Higher	Lower	Unidentate	(54)
11.	$Hg(OCOCF_3)_2$	1690	1416	274(12)	Higher	Lower	Unidentate	(55)
12.	$(PhCH_2)_3Sn(OCOCH_3)$	1618	1319	299(19)	Higher	Lower	Unidentate	(56)
13.	$[Co(OCOCF_3)_4](Ph_4As)_2$	1692	1421	271(20)	Higher	Lower	Unidentate	(57)
14.	$CaCu(OCOCH_3)_4.6H_2O$	1590	1410	180(4)	Higher	Almost the same	Unsym. Bridging Bidentate	(58)
15.	$[Cu(OCOCH_3)_2(H_2O)]_2$	1600	1425	175(21)	Higher	Higher	Sym. Bridging Bidentate	(59)
16.	$Li(OCOCH_3)(H_2O)_2$	1597	1435	162(22)	Higher	Higher	Sym Bridging Bidentate	(60)
17.	$[Mo(OCOCH_3)_2]_2$	1585	1440	145(23)	Higher	Higher	Sym. Bridging Bidentate	(61)
18.	$[Pd(OCOCH_3)_2]_3.0.5H_2O$	1600	1427	173(24)	Higher	Higher	Sym. Bridging Bidentate	(62)
19.	$[Rh(OCOCH_3)_2Py]_2$[b]	1590	1430	160(25)	Higher	Higher	Sym Bridging Bidentate	(25)
20	$Sb_2(OCOCH_3)Cl_2O(OH)$	1580	1435	145(26)	Higher	Higher	Sym Bridging Bidentate	(26)
21.	$Zn_4(OCOCH_3)_6O$	1639	1489	150(8)	Higher	Higher	Sym Bridging Bidentate	(63)
22.	$[V(OCOCF_3)_2C_6H_6]_2$	1720	1475	245(27)	Higher	Higher	Sym Bridging Bidentate	(27)
23	$Zn(OCOCH_3)_2tu_2$[c]	1577	1425	152(4)	Almost the same	Higher	Unsym Chelating Bidentate	(64)
24	$Cu(OCOCH_3)(Ph_3P)_2$	1565	1421	141(28,29)	Almost the same	Higher	Unsym. Chelating Bidentate	(65)
25	$Sn(OCOCH_3)_4$	1575	1440	135(8,30)	Almost the same	Higher	Unsym. Chelating Bidentate	(66)
26.	$NaUO_2(OCOCH_3)_3$	1537	1472	65 (31)	Lower	Higher	Sym. Chelating Bidentate	(67)
27.	$Mn(OCOCH_3)(CO)_2(Ph_3P)_2$	1520	1437	83 (32)	Lower	Higher	Sym. Chelating Bidentate	(32)
28.	$Zn(OCOCH_3)_2.2H_2O$	1550	1456	94 (5)	Lower	Higher	Sym. Chelating Bidentate	(68)
29.	$Re_2(CH_3)_2(OCOCH_3)$	1555	1450	105(33)	Lower	Higher	Sym Chelating Bidentate	(33)
	Only one compound, $Ru[OCOCF_3(CO)Ph_3P]_2[C_4HPh_2)$, has been crystallographically shown to contain chelating trifluoroacetato group but no ir data have been reported[34].							
30.	$Na(OCOCH_3)$[f]	1578	1414	164(35)	—	—	Ionic	
31.	$Na(OCOCF_3)$[f]	1680	1457	223(36)	—	—	Ionic	
32.	$K(OCOCF_3)$[f]	1678	1437	241(20)	—	—	Ionic	

a—Teta = C - Meso - 5,7,7,12,14,14 hexamethyl-1,4,8,11-tetraazacyclotetradecane

b—Py = Pyridine.

c—tu = Thiourea.

d—Using average values of ν(OCO) where necessary.

e—Not given.

f—Assumed ionic for infrared comparison.

directions of the shifts in $\nu_{asym}OCO$ and $\nu_{sym}OCO$ frequencies, is superior to the previously better-known ir criterion (Δcriterion) because in addition to its being applicable to all main types of carboxylate binding, it is also capable of making finer distinctions within the main types. The superiority

TABLE 2—INFRARED AND STRUCTURAL DATA FOR THE COMPOUNDS WHICH DO NOT FIT IN THE PRESENT CRITERION WITH POSSIBLE EXPLANATIONS

Sl. No.	Compound	$\nu_{asym}OCO$	$\nu_{sym}OCO$	Δ(IR)	Ref.	Directions of the shift in comparison to those in ionic acetate $\nu_{asym}OCO$	$\nu_{sym}OCO$	Mode of binding	Ref (Cryst. Struct.)	Explanations
1.	$[Co_2(OOCCH_3)(OH)L](H_2O)(EtOH)^a$	1565	1410	155	(37)	Lower	Almost the same	Unsym Bridging bidentate	(69)	Hydrogen bonding, two types of Co atoms are present
2.	$Ni(OOCCH_3)_2(H_2O)_2(Py)_2^b$	1550	1412	138	(38)	Lower	Almost the same	Unidentate	(70)	Hydrogen bonding
3.	$Me_3Pb(OOCCH_3)$	1550	1410	140	(39)	Lower	Almost the same	Unsym Bridging bidentate	(71)	—
4.	$Me_3Sn(OOCCH_3)$	1558	1418	140	(40)	Lower	Almost the same	Unsym. Bridging bidentate	(72)	—
5.	$[Ph_2Sn(OOCCH_3)_2]_2$	1530	1405	125	(41)	Lower	Lower	Sym. Bridging bidentate	(73)	Short M – M bond
6.	$[Cu(OOCCH_3)NH(CH_2)_2(NH_2)_2]ClO_4$	1550	1400	150	(4)	Lower	Lower	Syn.-Anti geometry	(74)	Acetate acts as a chelate as well as a bridge
7.	$[Pd(OOCCH_3)(Cl)(Me_2PhP)]_2$	1575	1418	157	(42)	Almost the same	Almost the same	Unsym. Bridging bidentate	(75)	Short M – M bond.
8.	$[Cr(OOCCH_3)_2(H_2O)]_2$	1575	1420	155	(3)	Almost the same	Higher	Sym Bridging bidentate	(76)	Hydrogen bonding
9.	$Os_2(OOCCH_3)_2(CO)_6$	1575	1465	110	(43)	Almost the same	Higher	Ciscoid bridging	(77)	CO groups distort the geometry
10.	$[Pd(OOCCH_3)C_3H_5]_2$	1575	1425	150	(44)	Almost the same	Higher	Unsym. Bridging bidentate	(78)	Short M – M bond
11.	$CrMo(OOCCH_3)_4$	1552	1459	93	(45)	Lower	Higher	Ciscoid bridging	(45)	Short M – M bond
12.	$[Pd_4(CO)_4(OOCCH_3)_4](AcOH)$	1555	1420	135	(46)	Lower	Higher	Sym. Bridging bidentate	(46)	Hydrogen bonding
13.	$Ni(OOCCH_3)_2.4H_2O$	1550	1425	125	(47)	Lower	Higher	Unidentate	(79)	Hydrogen bonding

a—H_2L=4-Hydroxy-3,5-bis[N-(2′-hydroxyphenyl)formimidoyl]toluene, b—Py=Pyridine

and validity of this criterion are further established by its having been derived from the study of, and hence applicability to, a very large number of compounds which do not belong to just one particular series or group.

The compounds listed in Table 2, however, do not observe the preceding relationships. For this there may be several reasons; pressure induced changes in KBr discs while taking the ir spectra, anion exchange while taking the high resolution spectra due to larger scanning time, hydrogen bonding effects, existence of polynuclear structures and short metal-metal bonds in the compounds are some of them. In seven of these compounds (1-7 in Table 2) the observed directions of the shifts in the frequencies of νOCO are of different types than observed in the relationships forming the basis of the present criterion; so even though the present criterion does not help in predicting or supporting their actual structure the shifts do not contradict the criterion. The remaining six compounds (8-13 in Table 2) have acetate binding different than would be suggested by the present criterion; their case is, therefore, problematic. However, closer examination indicates that five of them fall under one or the other category of possible explanations indicated above and are either dinuclear or polynuclear and the sixth one (13 in Table 2) need not be examined by any technique since the unidentate nature of the acetate binding is obvious from its composition.

This minor limitation, though cautions us, does not contra-indicate the proposed criterion. X-Ray diffraction crystallography, generally the most definitive source of information about the structural parameters for, and hence the nature of linkages in, chemical species, would of course be the most desirable technique to employ. Although it is becoming a routine analytical technique, it is still time and resource consuming. It is, therefore, best even in well-endowed laboratories to exhaust other, more conventional and easily accessible, approaches. The only conventional approach of wider applicability for the mode of carboxylate binding is ir spectroscopy and as is evident from the preceding discussion out of the ir criteria proposed so far, the present one has clearly an edge over the others.

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Carbon Fibres*

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1. The improvement in mechanical properties of materials has been generally centered on strength. With isotropic materials like many metals only strength can be improved; on the other hand with anisotropic materials like graphite and organic polymers both strength and modulus can be varied by changing prefered orientation. With depletion of natural mineral sources it is necessary to develop suitable alternative materials for various structural applications essentially to replace metals. The strength and modulus of graphite has made it a suitable substitute for structural materials with the attendant advantage of light weight.

1.1 *Carbon and Graphite*

The chemists and technologists, therefore, have tried various precursor materials for the production of carbon or graphite essentially for high temperature reactors, gas turbines, high speed aerospace vehicles, etc. The predominant factor holding further development is the limitation imposed by the mechanical and physical properties of currently available materials particularly for use at high temperatures[1]. The refractory nature and chemical inertness of carbon has proved valuable in applications such as insulators, packing materials, catalyst supports, electrical heating elements for special environments etc. In recent years an entirely new use has emerged for carbon fibres as an ablative material to resist very high temperatures developed on re-entry of space vehicles into the earth's atmosphere.

1.2 *Composites*

The most recent use for the carbon fibre reinforced plastics (CFRP) or oven metals is in the preparation of composites of exceptionally high specific stiffness and strength. The basic concept of fibre reinforcement[2] is the production of a two phase composite structure in which deformation of the matrix is used to transfer stresses by means of shear tractions at the fibre matrix interface to the embedded high strength fibres. Provided the length of the fibre is sufficient, the latter should then be constrained to take up the same deformation as the matrix over the greater part of their length and thus effectively reinforce matrix. Carbon or graphite fibre reinforced composites provide an equivalent stiffness to steel for only one-fifth of the mass and twice the stiffness of aluminium for only half the mass. With these properties, carbon fibre reinforced plastics find extensive applications in various vital fields such as aerospace, agriculture, sports engineering, medicine etc.

2. **Precursors for Carbon Fibres**

2.1 The pyrolytic decomposition of organic polymers provides a useful method of preparing special types and physical forms of carbon. In many cases the shape or physical form of the organic precursor is retained during high temperature treatment or carbonisation. This principle has been applied extensively in the preparation of carbon fibres from fibres of cellulose, rayon, poly-acrylonitrile and other polymeric materials. In general, the suitability of materials for the production of carbon fibres should satisfy the following basic requirements :

a. The fibrous form should be retained on pyrolysis, i.e. the material must not melt or deform when heated,

b The carbon skeleton should be capable of being readily changed into two dimensional graphite structure, and

c. The pyrolysis should take place without appreciable loss of volatile carbon compounds.

These requirements are satisfied by cellulose[3] and cross-linkable polymers such as polyacrylonitrile (PAN). The reason[4] for their high melting temperatures is that relatively strong intermolecular forces inhibit molecular motion. However, the cause of these forces are different in the two polymers – PAN and cellulose. In PAN, highly polar cyanide groups cause strong dipole-dipole forces to operate between molecules, whereas in cellulose the repeat unit, $\beta D(+)$-glucose unit, is a trihydric alcohol, so that the intermolecular forces result from hydrogen bonding interactions between hydroxyl groups and adjacent molecular chains.

The other potential candidate with promising prospects, both in price as well as in performance, are the pitch fibres. The pitch fibres are melt spun from Mesophase pitch derived from several sources like 'coal tar', 'PVC' pitch and 'coal'. Mesophase pitch is nothing but the liquid crystal state of pitch heated to temperatures above 350°. It is then melt, spun, thermoset and carbonised at temperatures of 1500-3000°[5,6].

The other polymeric precursor materials include lignin[7], polyvinyl alcohol[8], *p*-polypropylene[9], polyphenylene[10], phenol hexamine thermoset resin and a cured novolac phenolic resin[11], polyimides[12], pitch

* Acharya J. C. Ghosh Memorial Lecture (1977) delivered under the auspices of the Indian Chemical Society on 27th December, 1981 at Madras.

of polyvinyl chloride[13] etc. Attempts are also being reported for making carbon fibre directly from hydrocarbons[14].

Although these high performance and speciality fibres are called by the generic term carbon fibres, two types of such "carbon and graphite fibres", depending on the heat treatment temperatures have been identified :

Type I. Carbon fibre, 'High Modulus' — Well defined graphite structure with 99.9% carbon content is obtained when fibres are heated to 2000°. (Tensile strength 200-300 $\times 10^{3}$ psi ; Youngs modulus : 55-60 $\times 10^{6}$ psi).

Type II. Carbon fibre, 'High Strength' — The graphite crystals which are not well defined and with 90-98% carbon content are formed when fibres are heat treated to 1200°. (Tensile strength 350-450 $\times 10^{3}$ psi ; Youngs modulus · 35-40 $\times 10^{6}$ psi).

At high temperatures the order of graphitization in carbon layers increases and approaches ideal graphite structure. The layers glide down and the strength decreases.

2.2. *Cellulose*

The first successful material used for the production of carbon fibres is cellulose in its original form as well as in the regenerated form. It was Edison (1880) who developed carbon filaments from cellulose for incandescent lamps. The finite length of cellulose in its native form has led to the development of regenerated cellulose or rayon with improved physical and mechanical properties[15-18].

Tang and Bacon[19] carried out much useful work in the carbonisation of cellulose precursors. They proposed a multistage mechanism for the conversion of cellulose to carbon. The fibre undergoes physical and chemical changes during the heating cycle from 100° to the final stage of carbonization ; 700 to 1000°.

(*a*) *Pyrolysis : oxidation :*

Stage (i). Physical desorption of water (25-150°).

Stage (ii). Dehydration from adjacent H and OH groups of cellulose unit (150-240°).

Stage (iii). Thermal cleavage of the cyclic linkage and scission of C–O bonds and some C–C bonds via free radical reactions (240-400°) leading to formation of C, CO and CO_2 etc.

Stage (iv). Aromatisation at above 400° and formation of fused ring or ladder structures.

(*b*) *Carbonization and graphitization :* After pyrolysis the fibres are carbonized upto 1000° under tension[20-23]. The tension is to be increased for higher temperature, 2750°, so that an extension of 30(% takes place[24] and fibres with modulus of 50 $\times 10^{6}$ psi are obtained.

Disadvantages of this process are :

(i). It gives a low carbonization ; low yield of carbon fibre and takes long time for this. The theoretical weight loss in the process of carbonization is 55% ; but in practice the weight losses are 70-90%.

(ii). The cross-section is not of a regular shape but zig zag[25].

(iii) Stretching at high temperatures at 2250° involves high energy requirement and therefore uneconomical.

The development of carbon fibres from polyacrylonitrile fibres at low temperatures has led to replacement of carbon fibres from cellulose.

2.3. *Polyacrylonitrile* (PAN)

2.3 1 One of the most successful precursor materials for manufacturing high modulus and high orientation carbon fibres is PAN. It has an all-carbon backbone and gives greater yields of carbon than cellulose It stabilises when heated to 200 220° in oxygen The chemistry of the reactions in PAN pyrolysis are well studied and documented[26-29].

2 3 2. *Use of comonomers* · Most commercial PAN fibre precursors for carbon fibres contain comonomers, such as methyl acrylate (the most widely used), methyl methacrylate and vinyl acetate etc. These are copolymerized with acrylonitrile to increase the solubility of the co-polymer in various solvents such as DMF, DMAC, nitric acid etc. Small amounts of olefinic monomers are often included, usually along with a neutral monomer, to enhance dyeability. Although theoretically the strength and modulus of carbon fibres based on PAN homopolymer should be high, comonomers are used for ease of processing and solubility. This comonomer content is as high as 15% in the textile grade PAN while it is 6% for carbon fibres. Information is scanty regarding the effect of comonomers during the carbonization of PAN fibres. Fitzer and his co-workers[30-32a] have found that the optimum comonomer content around 3% is beneficial for both tensile strength and modulus of C-fibres.

2.3.3. *The processes* · The steps that lead to graphitization of PAN fibres are (a) oxidation, (b) carbonization and (c) graphitization.

The fibres are given a stretch before they are oxidised and cyclised at 70-100°. The ring closure takes place at a temperature of 100-220° leading to thermally stable polymer. Next stage is carbonization in inert atmosphere from 300-700°. Condensation and cross-linking takes place with the elimination of hydrogen cyanide, ammonia and water and

formation of hexagonal, possibly aromatic, structures. Beyond 700° upto 1000° fibres still contain 7% of nitrogen and some hydrogen but the type of physical and chemical bonding is not known. At 1500° carbon fibres of high strength are formed.

Graphitization in inert atmosphere takes place at ~1800-3000° with the elimination of all the elements other than carbon. Molecular re-arrangements take place giving graphite crystal structure resulting in high modulus fibres.

(*a*) *Oxidation :* Examination of these stages in detail reveal the importance of oxidation step which is to convert the acrylic polymer into a thermally stable ladder polymer.

It does not undergo chain scission reactions when heated strongly. Chain scission and related molecular disorientation would have catastrophic effect on the texture of the resulting carbon fibres and hence on their mechanical properties.

The cyclisation by which the ladder polymer is formed is the first reaction to occur after the acrylic polymer is heated above its second order transition temperature. The increased molecular motion allows the adjacent cyanide groups to approach close enough for reaction to occur between them induced by their dipoles. The new bond is formed after the migration of an electron pair from cyanide triple bond. In view of an effectively greater negative charge on the nitrogen atom, further ring closure occurs with corresponding ease.

Grassie[31] postulated that cyclisation can also be initiated by the presence of an acidic group which may be incorporated as the dye site.

The most important types of reactions during thermal treatment of PAN are 'dehydrogenation' and 'cyclisation'. Many investigators suggested the course of reactions in which cyclisation precedes dehydrogenation. The other possibility is based on the assumption that especially in the presence of air dehydrogenation occurs prior to cyclisation. From the results of other authors it can be concluded that cyclisation and dehydrogenation occur simultaneously. Fitzer and Muller[32] from the IR and DTA measurements favour the combined mechanism with dehydrogenation preceding cyclisation. They conclude that at the end of cyclisation the dehydrogenation is not complete.

Watt and Johnson[33] oxidised two sets of fibres — one, terpolymer with 95, 4.6 and 0.4 mol % of acrylonitrile, methyl acrylate and vinyl acidic compound (vinyl acidic compound is added to act as a dye site) ; the other, a copolymer with 95.4 and 4.6% of acrylonitrile and methyl acrylate. When they were oxidised as such the oxygen uptake with time was very poor in the case of the second without acidic comonomer as compared to the first with acidic comonomer. When they were vacuum preheated and then oxidised, the first one did not show any improvement on oxidation with regard to oxygen uptake whereas the second copolymer showed a marked increase in the oxygen uptake. These clearly show that the carboxyl containing group definitely plays a key role in aiding cyclisation. These results are seen in terms of oxygen uptake with oxidation in air at 230° when Courtelle and Orlon fibres are compared. When they are vacuum pre-heated and then oxidised, Courtelle fibre did not show much difference in oxygen uptake but Orlon did. This shows that in the Courtelle fibre the oxidation, the cyclisation and ladder structure formations are aided by the carboxyl comonomers during vacuum preheating stage.

The oxidation step is a very important one as it produces an oxidized polymer structure approximately parallel to the fibre axis which may be regarded as a template for the formation of oriented carbon fibre.

To obtain quality material it is necessary to control this polymerization through oxidation and stabilization[27,30].

Chemical reactions involved during oxidation are

(i). initiation of nitrile polymerization,

(ii) propagation of nitrile polymerization,

(iii). oxygen uptake,

(iv). dehydrogenation, and

(v). minor loss of volatile materials.

The exact structure of this oxidised polymer is not clear although lot of work has been carried out. The infrared spectrum[34] shows the disappearance of –C≡N– and formation of –C=N–C=N– conjugated double bonds The differential thermal analysis shows decreased exotherm with the formation of partially oxidised films indicating that the stabilization is achieved by oxidation and cyclization.

The significant contribution is due to Shindo[26] who thought that oxidation preceded carbonization. Watt, Philips and Johnson[27] introduced the concept of holding the fibre under controlled tension during the oxidation stage. This meant the necessity to maintain alignment of the original polymer molecules prior to carbonization, and therefore attainment of truly high strength, high modulus fibres during oxidation itself without the need for stretching during graphitization stage.

(*b*) *Carbonization* After oxidation the fibre is slightly reduced in diameter and becomes black. Fibres are carbonized under load (tension) over many hours to 1500° to drive off most elements other than carbon. The small molecules like NH_3, HCN and H_2O are removed and high strength fibres result.

(*c*) *Graphitization :* For type I carbon fibres the graphitization temperature is usually from 1800 to 3000° in the presence of argon. There is an increase in the prefered orientation of the crystallites with increasing graphitization temperature which accounts for the increased motion.

In order to improve the strength and modulus of carbon fibres Moreton and Watt[38] carried out spinning of PAN fibres under clean room conditions in order to minimise the impurities which deter the carbon fibre properties. They stipulated the clean room condition to less than 100 particles/ft^3 which could be achieved using laminar flow filters above the spinning zone. Johnson and Thorne[40] have investigated the fracture surface of carbon fibres with SEM and concluded that impurities in the PAN precursor were the main cause of flaws in carbon fibre.

Some interesting research findings have been reported recently[36] revealing the production of carbon fibres from PAN at low temperatures such as 600-900°. In the process it is described that the resulting carbon fibres possess strength with nearly twice the tensile strength as compared to the old process in that temperature range. The process consists of giving PAN fibres a pre-treatment with molten benzoic acid at 175° and acetylene prior to the oxidation step. This is referred to as 'modified process'. Exhaustive fundamental work has to be done before it could take a firm standing to replace the old method.

A good amount of fundamental work on the aspects of oxidation, carbonization and graphitization are reported[37-45]. The structure of PAN fibre is due to Bennett and Johnson[46].

The work of Rolls Royce highlighted a number of important aspects associated with the heat treatment stages.

THE FORMATION OF CARBON FIBRE. SEQUENCE OF EVENTS THROUGH HEAT TREATMENT

Process	Temperature	Event
Oxidation in air	70-100°	Molecular relaxation at glass transition temperature prevented by securing fibres to rigid frame
	100 220°	Cyclisation and oxidation reactions leading to thermally stable ladder polymer.
Carbonization in inert atmosphere	300-700°	Condensation and cross-linking reactions with the elimination of hydrogen cyanide, ammonia and water, and the formation of hexagonal, possibly aromatic structures.
	1000°	Fibres still contain 7% nitrogen and some hydrogen but the type of physical/chemical bonding is not known.
	1500°	Carbon fibre type II.
Graphitisation in inert atmosphere	1800-3000°	Elimination of all elements other than carbon. Molecular re-arrangement giving graphite crystal structure. Carbon fibre type I.

2.4. *Other precursors for carbon fibres*

The search for a precursor that is cheap in cost and abundant in availability has been the requirement for carbon fibres in numerous applications. Because of these considerations it provided impetus to work on pitch based carbon fibres. The work on pitch fibres was started in Japan[47-49] where carbon fibres of low modulus and strength were produced at earlier stages. Union Carbide has produced pitch based carbon fibres which appear to pose as a competitor for the PAN based one. However, it will take few more years for the pitch based precursor to become a potential competitor for PAN fibres.

PVC was one of the first starting material for the pitch based carbon fibres. Ottani[49] produced pitch from PVC by heating the latter in nitrogen atmosphere at 400° for 30 min. The carbon fibres were melt spun from pitch which softend at 150° and turned into viscous liquid at 200°. Apart from PVC[46], coal tar[50] and coal[51] are used as starting materials for pitch based carbon fibres.

The Union Carbide improved the position of pitch based carbon fibres by introducing a process wherein coal tar pitch is made use of instead of the PVC pitch. In this process coal tar pitch is heated to a stage of converting pitch partly to a liquid crystal or mesophase state which occurs during pyrolysis between 350-500°. From the mesophase, the fibres are melt spun and carbonized and graphitized subsequently. The structure of mesophase from electron micrographs (the EM pictures of the anisotropic mesophases formed in isotropic petrol pitch by that treatment at 400°) and the model of the liquid crystal mesophase which consists of plannar polyaromatic molecules[52] are interesting. Mesophase spherules are formed by orientation of poly condensed aromatic hydrocarbons along lamellae and by accumulation in layers. As they already have high order in the mesophase stage, when drawn in such a stage the fibres possess high Young's modulus.

Union Carbide has placed in the market Thornel type P, Thornel 50 and Thornel 300. There are several recent references that outline the carbon fibre production from coal through the process of solvolysis liquefaction of coal. The pre-treatment of coal involves milling and sieving it to a fine powder. It is extracted with benzene and the benzene insoluble portion is heated at a rate of 10°/min upto 350°. This contains 95% neo-mesophase pitch. Refined pitch in its mesophase form is melt spun, oxidized, carbonized and strain graphitized to produce carbon fibres. The comparison between the PAN and pitch based carbon fibres show that the latter possess inferior tensile strengh. However, the results reported by Bacon[53] recently throw light on the improvement of strength comparable with PAN based carbon fibres by eliminating the structural flaws. Cost wise, the carbon fibres from pitch show an edge over the PAN based carbon fibres – 1 lb. of high strength and high modulus carbon fibres from PAN cost $35/lb to $125/lb, while that of carbon fibres from pitch of comparable strength and modulus cost[54] only $20/lb. With the increase in production the cost may still come down. The pitch fibres have an added advantage of having 80% of yield of carbon as compared with

PAN which has only 50% and hold good promise for future as precursors for carbon fibres.

The processes for manufacture of carbon fibres from the three precursors—cellulose, PAN and pitch are therefore very interesting.

2.5. *Development of suitable precursors at CLRI*

Acrylonitrile and its copolymers are found to be better precursors because of their unique property to form ladder type of structure and high carbon yield. In the textile grade PAN the comonomer content is high which is not advantageous for carbon fibres for composites[52a]. The production of special grade PAN fibre is controlled by several international patents and is a closely guarded secret by the fibre manufacturers. Hence it is necessary to develop a suitable method for the development of acrylic copolymers with more than 90% acrylonitrile with various comonomers.

The presence of oxygen containing monomers in the copolymers of PAN facilitate oxidation and carbonization. Hence a variety of copolymers containing 3-15% comonomers were prepared

(a). Polyacrylonitrile-co-methyl acrylate,
(b). Polyacrylonitrile-co-butyl acrylate,
(c). Polyacrylonitrile-co-vinyl pyrrolidone,
(d). Polyacrylonitrile-co-vinyl acelate,
(e). Polyacrylonitrile-co-methyl mataacrylate.

Using laboratory devices these polymers were tested for their spinnability and carbonization characteristics and 'a' has been identified as a potential candidate.

3. Fibre spinning

3.1. The spinning of the PAN copolymers can be done by both wet and dry spinning processes. In the 'wet spinning' the copolymer is dissolved in a suitable solvent such as DMF, DMSO, DMAC or nitric acid and spun through the corresponding dilute solution of the solvent in water and subsequently subjected to washing and stretching. In the 'dry spinning' process, the copolymer is dissolved in solvents such as DMF or DMAC and hot air is blown through the fibres emerging from the spinnerette face to remove the solvents. The solidified fibres are then subjected to further stretching before being collected on frames. An improved form of wet spinning of acrylic fibres is to hold the spinnerette one cm above the coagulation bath. This method called 'dry jet wet spinning' produced more oriented and compact structure[54].

Fundamental studies such as effect of coagulation bath temperature, molecular weight of the copolymer and additives on the mechanical properties of precursor (PAN fibre) have been carried out at CLRI besides spinning fibres for carbonization. The polymers made were characterized by GPC, viscosity, elemental analysis and X-ray diffraction methods and the spinning conditions were fixed for each polymer depending on the solubility and molecular weight using a mechanical spinning assembly (Fourne, West Germany).

3.2. *Effect of coagulation bath temperature*

The temperature of the coagulation bath was varied from 10 to 50° and the minimum fibre breakage and better mechanical properties were obtained[55] when the coagulation bath temperature was low.

EFFECT OF BATH TEMPERATURE ON PRECURSOR AND CARBON FIBRE

Sl. No.	Bath temp. °C	Stretch ratio	Precursor		Carbon fibre	
			T S $\times 10^3$ psi	M $\times 10^6$ psi	T.S. $\times 10^3$ psi	M $\times 10^6$ psi
1.	10	1 : 8	85	1.4	140	18
2.	20	1 : 8	75	0 9	85	14
3.	30	1 : 8	51	0.8	63	—

3.3. *Effect of molecular weight*

Variation of polymer molecular weight and the consequent distribution by change of the polymerization temperature was studied. The polymers were analysed by viscosity and GPC The GPC data clearly indicated the narrow molecular weight distribution for the low temperature polymer and spreading of molecular weight at higher temperature[55a]. Effect of molecular weights on fibre properties is also very striking.

VISCOSITY AND GPC ANALYSIS OF THE POLYMERS PREPARED AT DIFFERENT TEMPERATURES

Sl. No	Polymer	Viscosity	Elution volume
1.	P_1^*	2.55	51
2.	P_2	1.965	5C, 58.5, 68
3.	P_2	1 10	51, 55,59
4	P_4	0 95	52, 56,60.5

EFFECT OF MOLECULAR WEIGHT ON FIBRE PROPERTIES

Sl. No	Polymer	Stretch ratio	Diameter	T.S. $\times 10^3$ psi	Modulus $\times 10^6$ (psi)
1	P_1	1 : 10	16	73	1.02
2.	P_2	1 . 8	18	64	1 12
3	P_3	1 6	22	55	1.10
4.	P_4	1 : 5	25	45	0.80
5	P_5	1 : 5	28	29	0.60

PROPERTIES OF PAN-CO-MA OF DIFFERENT MOLECULAR WEIGHTS

Polymer	Intrinsic viscosity (η) dl/g	Elution volume ml	Maximum solubility	Precursor		Carbon fibre	
				T.S. $\times 10^3$ psi	M $\times 10^6$ psi	T.S. $\times 10^3$ psi	M $\times 10^6$ psi
P_1	2.550	51	12 14	68.66	1 08	104	20.8
P_2	1.965	50, 58.5, 59	19.0	51.68	0.804	60	14.92
P_3	1.110	51, 55, 59	22.0	49.50	0.790	85	19.C0
P_4	0.95	52, 56 60.5	27.0	36 88	0 485	100	10.00

* P_1, P_2, P_3 and P_4 are prepared at 35, 45, 50 and 60° respectively.

3.4 *Effect of additives, solvents etc. on fibre properties*

Maximum concentration[56] of the polymer in the dope is preferred to minimise the voids in the fibres, which are generally drawn from solution of

low dope concentrations. To facilitate the spinning processes conditions like deaeration, extrusion, increase in solid content, dope viscosity modifiers like aryl or alkyl secondary amino hydrochlorides have been made use of[57]. The coagulation bath consists of DMF and water at varying proportion and the optimum concentration has been fixed at 50% DMF-water.

Wet spinning is a three component system of polymer, solvent and non-solvent in which two transitions, namely gelation and phase separation, occur. Kinetically, gelation is no doubt a slow process compared to phase separation but it is not always possible to design conditions so that the phase separation could be preceded by gelation. However, gelation rate is sensitive to temperature, hermal history and additives. A few studies on he effect of additives to produce gelation during spinning were carried out[51]. For this purpose, a non-solvent and a gelling agent – an inorganic compound – are made use of. The effect of these additives produced interesting results on the cross-section of fibres not reported earlier. All the spinning conditions being the same, the cross-section of the fibre is 'bean' shaped when an organic additive is added. When an inorganic additive is added, the cross-section is almost 'round'. Same is the case n the case of addition of non-solvent and without ny additive[58]. Looking at the mechanical properties[59] of the fibre, the tensile strength and Young's modulus are minimum when an organic dditive is added and maximum when an inorganic dditive is added. In the case of non-solvent and without additive, the values are almost the same. When a mixture of all the additives is added, the ensile strength and modulus are definitely more han those obtained without any additive and in he presence of non-solvent and an organic dditive

The round shape of the fibre is due to the ifference in diffusion of solvent and non-solvent hrough the solidified skin of the fibre after oagulation and the rate at which such diffusion ccurs. A similar situation has been encountered[54] n the case when HCl or acetic acid or oxalic cid is added to the spinning bath whereby the H of the spinning bath varies from 2.3 to 7. When he *p*H of the bath solution is less than 3, the fibre ttained bean structure whereas at *p*H 6 it was ound. An attempt was made to study the effect f *p*H of the dope solution and it was found that hen an organic additive is added the *p*H is 4.15 here the bean shaped cross-section of the fibre as observed[60].

When an inorganic additive is added the cross-ectional shape is round at the *p*H 11.96 and in the ase of non-solvent the *p*H of DMF (used for aking dope solution) is 11.5. These values show learly that the cross-sectional shape of the fibre dependent on the *p*H of the DMF solution used or preparing the polymer dope. When it is acidic is bean shaped and when it is basic or neutral it round shaped.

Effect of Additives on the Properties of PAN–CO–MA

Additive	Concentration %	Elongation %	T.S. × 10^3 psi	Modulus × 10^6 psi	Shape of the fibre
A_1 (organic)	0.5-5	5.7	26.35	0.6	Bean
A_2 (inorganic)	0.1-2	4.9	46.28	1.2	Round
A_3 (non-solvent)	0 1-1	5.7	34.17	0.7	Round
O(without additives)	...	6 6	36.02	0.75	Round
M(mixture of all additives)		5 7	48.98	1.00	Bean

*p*H Values of DMF and Additive Solutions

Solution	*p*H
DMF	11.7
DMF+1% water	11.5
DMF+55-45% water	7.8
DMF+Organic salt	4.15
DMF+Inorganic salt	11.96

The stretch baths mainly consisted of water. Water acts as plasticizer during stretching of the fibre With the hydrophobic repulsion of the fibre it might be surprising to see plasticizing action of water. But once free volume has been created by strain or temperature to allow entrance of water into the fibre, it acts as strong plasticizing agent. Plasticization here is meant to denote decrease in the resistance of the fibre to an imposed stress by the liquid water Plasticization is governed to some extent by the molecular volume and dipole moment of the liquid. Hence, to increase plasticization some amount of DMF is also added to water in the stretch baths After the fibre passes through the stretch baths, the DMF content in the fibre is considerably reduced but the fibre looks porous Passing over to the godet heater, the fibre undergoes collapse process, the porous nature of the fibre is eliminated and the porous structure is no longer evident. This is influenced by the moisture content in the fibre, temperature of the godet heater and time of contact of the fibre

Considerable efforts were put forth to improve the fibre properties by changing the conditions of spinning and a second stage hot stretching above

Properties of CLRI Acrylic Precursors

Sl. No	Diameter	Tensile strength × 10^3 (psi)	Modulus × 10^6 (psi)
1.	17 5	99.5	1.17
2.	20 0	103.7	2.24
3.	18.25	103.33	0.699
4.	18.5	104.74	1.809
5.	—	104.2	0.761
6.	17.0	105.77	1.450
7.	—	107.07	1.075
8.	18 75	109 62	2.342
9	—	112.0	1.125
10. (Torray)	12.14	80.0	1.1
11. (Dolan)	14	76 0	1 0
12. (Beslon)	13	85.0	1.1
13. (Hercules)	13	37.42	0.78

100° using different stretch baths separately. The fibre properties improved and in certain cases excelled even over the imported fibres.

Some of the fibres have been carbonized at 10 0° and the properties of such carbon fibres are comparable to those obtained from imported PAN fibres under similar conditions.

PROPERTIES OF CARBON FIBRES FROM CLRI PRECURSORS

Sl. No.	Tensile strength $\times 10^3$ (psi)	Modulus $\times 10^6$ (psi)	Carbon yield
1	46.77	1.26	–
2.	57 59	5.80	54
3.	62.70	1.56	—
4.	62 66	1.81	—
5.	62.70	10.72	—
6	70.80	13.53	52
7.	76.80	12.98	—
8.	77 70	10.12	–
9.	86.66	12 15	51
10	93 09	18 61	59
11	94.20	19.58	—
12	98.50	20.00	54.25
13	100 00	20.20	51
14	104 5	10 30	56 5
15	175.4	22.95	–
16.	188.0	19 18	—

Considerable improvement could be achieved by reducing the diameter of the precursor fibres during the second stage of hot drawing as well as spinning under clean room conditions.

4 Applications of carbon fibre reinforced plastics

There remains, no doubt, that carbon fibre reinforced polymers (CFRP) with their extremely high stiffness and low density will replace metals in most future applications where weight saving is the main goal The only problem is that manufacturing of cars from metal is highly rationalized in industrialized countries, whereas the present production methods of composites still causes high labour costs. Carbon fibre is available in the market in different forms, such as mats, tapes, free fibre in a tow, chop strand mats, felts, springs etc The recent applications of CFRP are in the aeroplanes and aerospace vehicles. The composite technology offers therefore a great chance for developing countries with high labour capacity.

In human surgery also, carbon fibre reinforced composite will play an important role in future. Bone plates in osteosynthesis[61-63] are one example because of the possibility to tailor the mechanical properties and thus to match the special need controlled by the elastic behaviour of bones. In case of CFRP as material for tools in surgery, one utilises the additional advantage that neither carbon nor polymers absorb X-rays and improved X-ray images can be taken *in situ* during operation. The isotropic form of polymeric carbon, the glossy carbon, is a corrosion resistant impervious material. This material is used in human medicine because of its outstanding bio-compatibility, as electrodes, percutaneous leads, dental and joint implants. The most striking success of monolithic carbon is achieved with its application as heart valve components. The anisotropic form of polymeric carbon fibres can be applied for replacement of ligaments and tendons. The inferior variety of carbon fibres find their use in the manufacture of sports goods like badminton and tennis racquets, golf clubs and racing bicycles.

5. Future projection

Carbon fibres can be produced in a number of ways from a variety of starting materials and their character is strongly influenced by the manufacturing techniques employed. The demand for carbon fibres is growing apace, both in terms of quantity and area of application Consumption is currently around 450 tonnes/year increasing at approximately 50 per cent per year The world market is likely to reach 1000 tonnes/year in 1981-82 and the prospects thenceforth look extremely good[64]. Continued development in aerospace and industrial use is likely to push annual production requirements upto several thousand tonnes. Production is located mainly in three countries, viz. Japan, USA and UK with 40 per cent world output from USA.

India today ranks foremost among the developing countries in resin production Until 1955, phenolic moulding powder was the only raw material made in India. Today, we have several units for the production of various types of plastics such as polyethylene, polyester, nylon etc. At present a large scale utilisation of these plastics are envisaged for the production of composites. It is imperative that the chemists and technologists should jointly venture for new application of reinforced plastics for various applications. It is the chemist's part to develop suitable precursor materials and the technologists part to design suitable processes for the production of carbon fibres for various applications.

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Mixed Chelate Complexes of Iron(III) Containing Dithiocarbamate and Acetylacetonate, Oxinate or Glycinate

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Six compounds of the types $Fe(dtc)_2(AA')$ and $Fe(dtc)(AA')_2$ were isolated by reacting iron(III) salt with sodium salt of diethyl-dithiocarbamic acid (Nadtc) and acetylacetone/8-hydroxyquinoline/glycine (AA') in stoichiometric ratio. The compounds were characterized on the basis of their analyses, molar conductance, magnetic susceptibility, infrared, ultraviolet spectral data and molecular weight measurement. All the compounds were found to be six-coordinated with presumably distorted octahedral configurations.

SYNTHESIS and characterization of a number of mixed chelate complexes of manganese(II and III)[1,2], cadmium(II) and nickel(II)[3], and copper(II)[4] have been reported from this laboratory. Keppert[5] has predicted that the normal geometries of the compounds experience distortion as the 'bite' of the bidentate ligands changes. With this back-ground, the preference of co-ordination number and nature of co-ordination by bidentate ligands such as diethyl-dithiocarbamate(dtc), acetylacetonate(acac), oxinate(ox) and glycinate(gly) around iron(III) is reported in the present communication.

Preparation of complexes :

Preparation of $Fe(dtc)_2(acac)$ and $Fe(dtc)_2(ox)$: Ethanolic solution of ferric chloride, sodium salt of diethyldithiocarbamate and acetylacetone/oxine were reacted in 1 : 2 : 1 molar ratio. Alcoholic solution of sodium acetate was added to it till the compounds separated out which were filtered, washed with ethanol, ether and dried *in vacuo*.

Preparation of $Fe(dtc)(acac)_2$ and $Fe(dtc)(ox)_2$. These compounds were obtained by the same method as above by reacting $FeCl_3$, Nadtc and acacH/oxH in 1 : 1 : 2 molar ratio.

Preparation of $Fe(dtc)_2(gly)$ and $Fe(dtc)(gly)_2$: To an ethanolic solution of ferric chloride was added a mixture of ethanolic solution of sodium salt of diethyldithiocarbamate and aqueous solution of glycine in stoichiometric ratio. The compounds separated out on stirring which were filtered, washed with ethanol, ether and dried *in vacuo*.

Experimental

All the chemicals used were of AnalaR grade. Analyses of iron and sulphur by standard methods were consistent with the formulations of the compounds. Infrared spectra were recorded in nujol mulls on SP-200 and Perkin Elmer spectrophotometers. Electronic spectra were recorded on SP-500 spectrophotometer. Magnetic susceptibility measurements were carried out by a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant. The diamagnetic corrections were calculated by using Pascal's constants[6]. The conductance measurements were carried out in $\sim 10^{-3} M$ nitrobenzene solution using Systronics direct reading conductivity meter 303. The molecular weight measurements were carried out by Rast method using camphor as solvent. The relevant analytical, molar conductance and magnetic susceptibility data of the compounds are given in Table 1 and infrared spectral data are recorded in Table 2.

Results and Discussion

The low values of molar conductance (~ 2 ohm^{-1} cm^2 $mole^{-1}$) *in nitrobenzene medium* (Table 1) indicate that the compounds are non-electrolytes. The high-spin iron(III)(S=5/2) with $3d^5$ configuration is expected to exhibit magnetic *moment of 5.92 B.M which should be temperature* independent, as the ground term is $^6A_{1g}$. On the other hand, the low-spin iron(III) with $^2T_{2g}$ term, which is dependent on temperature, is expected to exhibit magnetic moment slightly higher than the spin-only value of 1.73 B.M. but less than ~ 2.5 B.M. The reported experimental values of magnetic moment of iron(III) for both $^6A_{1g}$ and $^2T_{2g}$ terms generally respond to the theoretical values. But the dithiocarbamate complexes of iron(III) were found to exhibit magnetic moment values intermediate between spin-free and spin-paired configurations[8,9]. Three compounds under present investigation viz., $Fe(dtc)_2(ox)$, $Fe(dtc)(ox)_2$ and $Fe(dtc)_2(gly)$ were found to exhibit magnetic moment values of 6.07, 5.93 and 6.07 B.M. as expected for $^6A_{1g}$ term. The other three compounds viz., $Fe(dtc)_2(acac)$, $Fe(dtc)(acac)_2$ and $Fe(dtc)(gly)_2$ were found to exhibit magnetic moment values (3.28-4.09 B.M., Table 1) intermediate between the spin-free and spin-paired configuration as suggested by Figgis and Lewis[9]. Of course, polynuclear complexes were also found to exhibit similar abnormal magnetic moment values.

TABLE 1—ANALYSIS, MAGNETIC SUSCEPTIBILITY AND MOLAR CONDUCTANCE DATA OF MIXED CHELATE COMPLEXES OF IRON(III)

Complexes (Colour)	m.p. °C	%Fe Found (Calcd.)	%S Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)	μ_{eff} in B.M.	Λ_m(mhos)
1. $Fe(dtc)_2(acac)$ (dark brown)	260	12.09 (12.37)	24.38 (26.41)	17.90 (18.60)	4.50 (4.69)	3.68	2.0
2. $Fe(dtc)(acac)_2$ (brown)	255	12.90 (13.38)	16.10 (15.94)	32.60 (32.80)	5.91 (6.01)	4.09	1.0
3. $Fe(dtc)_2(ox)$ (black)	238	11.29 (11.25)	22.21 (25.88)	25.92 (26.58)	5.66 (5.88)	6.07	2.0
4. $Fe(dtc)(ox)_2$ (grey)	263	11.77 (11.84)	12.92 (13.02)	45.52 (46.29)	5.25 (5.78)	5.98	2.0
5. $Fe(dtc)_2(gly)$ (dark brown)	263	13.09 (13.09)	29.58 (30.07)	11.02 (11.25)	8.59 (9.06)	6.07	1.9
6. $Fe(dtc)(gly)_2$ (blackish brown)	268	15.68 (15.85)	18.72 (18.20)	16.83 (17.05)	7.05 (7.25)	3.28	1.8

TABLE 2—INFRARED SPECTRA OF MIXED CHELATE COMPLEXES OF IRON(III)

	dtc			acac		ox	gly		
	ν(C=N)	ν_{as}(C−S)	ν_s(C−S)	ν(C=O)	ν(C=C)	ν(C−O)	ν_s(COO)	ν_{as}(COO)	$\nu(NH_2)$
$Fe(dtc)_2(acac)$	1495 vs	995 s	710 s	1600 vs	1540 s	–	–	–	–
$Fe(dtc)(acac)_2$	1495 s	995 s	720 vs	1630 m	1540 w	–	–	–	–
$Fe(dtc)_2(ox)$	1505 s	1025 s	735 w	–	–	1100 vs	–	–	–
$Fe(dtc)(ox)_2$	1510 s	1005 s	720 s	–	–	1105 vs	–	–	–
$Fe(dtc)_2(gly)$	1500 w	1000 w	720 s	–	–	–	1375 w	1665 w	3350 w
$Fe(dtc)(gly)_2$	1500 w	990 w	715 s	–	–	–	1370 w	1665 w	3350 w

s = sharp, vs = very sharp, w = weak, m = medium.

But the molecular weight measurements of the complexes (not given in the Table) indicate that they are monomers. Mitchell and Parker[10] have suggested that the most plausible explanation of such magnetic properties is the presence of iron(III) in spin state $S=3/2$, because the low magnetic moment cannot be explained by interactions between the iron atoms and must therefore be due to a change of spin state of iron. The most acceptable spin state in such a case is $S=3/2$ (spin-only moment 3.87 B.M.).

Infrared spectra : The infrared spectral bands of the complexes with their tentative assignments are given in Table 2. The ligand dithiocarbamate was known to behave as a bidentate or a monodentate one. The former exhibits ν_{as}(C−S) near 1000 cm^{-1} as a single band whereas the latter shows a doublet in the same region[11]. Also, the ν(C=N) of the former (above 1485 cm^{-1}) is higher than that of the latter (below 1485 cm^{-1})[12]. In the present case, the ν_{as}(C−S) band at $\sim$1000 cm^{-1} (Table 2) was obtained as a single band and ν(C=N) band was found above 1485 cm^{-1} (Table 2) in all the compounds indicating that diethyl dithiocarbamate is co-ordinated to iron(III) as uninegative bidentate ligand in each case. Infrared spectra of acetylacetonato complexes have been studied extensively. The ligand acetylacetone can co-ordinate either as uninegative bidentate through its enol form, neutral bidentate through the keto form, or neutral monodentate through carbon atom. In the case of enol form co-ordination, the ν(C=O) and ν(C=C) bands are found at 1577 and 1529 cm^{-1}, respectively[13,14] whereas the strong band due to ν(C=O) is obtained near 1700 cm^{-1} when it is co-ordinated through keto form[14]. It was found[16] that for carbon bonded complexes, the ν(C=O) were higher and ν(C−C) were lower than those of the oxygen bonded compounds. In the two acetylacetonato chelates of iron(III), the ν(C=O) band was found at 1600 cm^{-1} and ν(C=C) at 1540 cm^{-1} (Table 2) indicating that the ligand was co-ordinated to the metal atom as an uninegative bidentate one. Similar observations were also reported by Graddon[17]. Charles *et al*[18] have reported that in case of oxinate complexes of metals, the ν(C−O) was obtained at 1120 cm^{-1} region, the position of the band slightly varying with the metal. In the present case, the ν(C−O) band due to oxine was found at 1100 and 1105 cm^{-1} (Table 2) indicating the co-ordination of the ligand through nitrogen and oxygen atoms as uninegative bidentate one. The $\nu_s(COO^-)$, $\nu_{as}(COO^-)$ and $\nu(NH_2)$ bands due to the ligand glycine, observed at $\sim$1370, 1665 and 3350 cm^{-1} respectively, indicate that it is co-ordinated to the metal atom as an uninegative bidentate one. It has been found[19] that in the case of bidentate nature the glycine group absorbs at 1643 cm^{-1}, unlike either the ionised monodentate group (1610 cm^{-1}) or the unionised monodentate group (1710 cm^{-1}).

The studies of electronic spectra of the complexes are consistent with the octahedral nature of the compounds. The bands obtained at $\sim$14700, $\sim$19600 and $\sim$23000 cm^{-1} may be assigned to the

transitions ${}^6A_{1g}\rightarrow{}^4T_{1g}$, ${}^6A_{1g}\rightarrow{}^4T_{2g}$ and ${}^6A_{1g}\rightarrow{}^4E_g$, respectively as suggested by Ballhausen[20] and Balt *et al*[21]. Also as suggested by Kepert[5], the regular octahedral stereochemistry would experience distortion due to the presence of chelating agents that too of a dissimilar nature. Hence, it is concluded that the six compounds reported here are mixed chelate complexes of iron(III) possessing distorted octahedral geometry.

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Phenylmercury(II) Compounds-II. Some Novel Three-Coordinate Phenylmercury(II) Complexes with Triazene-1-Oxides

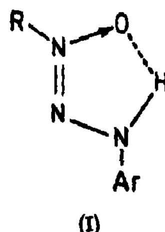
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Triazene-1-oxides (TH) react with phenylmercuric acetate to form phenylmercury(II) complexes of the general formula [C_6H_5.Hg(T)] All these complexes are monomeric in freezing benzene. Their structures have been deduced from elemental analyses, conductance, molecular weight and infrared spectra. These complexes have three-coordinate Hg(II) with the ligands functioning as monobasic chelating bidentate ligands.

COORDINATION complexes of triazene-1-oxides with several transition metal ions have been studied by many workers[1-6]. We report in this paper a series of phenylmercury(II) complexes with triazene-1-oxides (I) which are shown to have three-coordinate Hg(II).



(I)

Experimental

Materials : Ligands were synthesised by following published procedures[1]. Phenylmercuric acetate was prepared according to the procedure given in the literature[7].

Synthesis of phenylmercury(II) compounds : 0.002 mole of phenylmercuric acetate was dissolved in hot ethanol (~25 ml) and filtered into an ethanolic solution (~15 ml) of 0.002 mole of the ligand. The mixture was refluxed for 15 min and cooled to room temperature. Yellow needle-shaped crystals separated out which were collected on a filter and recrystallised from ethanol.

Similar procedure was adopted for the synthesis of the complexes of the ligands : 3-*p*-tolyl, 1-phenyl triazene-1-oxide.

For the complexes of 3-*p*-chlorophenyl, 1-methyl triazene-1-oxide, 3-*p*-tolyl-1-methyl triazene-1-oxide and 1, 3-diphenyl-triazene-1-oxide the refluxed solution had to be concentrated to a small volume (~10 ml). The complex of 3-*p*-nitrophenyl 1-phenyl-triazene-1-oxide separated out readily and was recrystallised from acetone.

Elemental analyses and physical measurements Carbon and hydrogen analyses were performed b M/s. Alfred Bernhardt Micro-analytische Labor torium, West Germany. Nitrogen was estimate by Dumas method and mercury was determined b following our procedure[8] (Table 1). Conductanc was measured with a Philips PR 9500 Bridge. I spectra were run at C. D. R. I., Lucknow. Molecula weights were determined by cryoscopic metho using benzene. Characterisation data of pheny mercury(II) complexes of triazene-1-oxides an their molecular weights in benzene appear i Table 1.

Results and Discussion

All these complexes are crystalline, highl soluble in chloroform and acetone and moderatel soluble in benzene, ethanol and methano They have very low molar conductance valu (0-1 $ohm^{-1}cm^2mole^{-1}$) which indicates that th complexes are nonelectrolytes. These complexe are monomeric in freezing benzene (Table 1).

IR spectra · The expected ir bands for $\nu_{(N-H}$ (3150-3200 cm^{-1}), $\nu_{(N=N-N)[sym\ triazene]}$(1510-146 cm^{-1}) and $\nu_{(N\to O)}$(1310-1295 cm^{-1}) have all bee found in the ir spectra of the triazene-1-oxid ligands[9-14].

The N→O stretching bands of all the pur triazene-1-oxides appear in the region ~1295-131 cm^{-1} and get shifted to lower frequency in th region ~1230-1245 cm^{-1} in their phenylmercury(I complexes which suggests that oxygen atom i coordinated to phenylmercury(II). This very shar band (~1230-1245 cm^{-1}) also covers a few wea bands in this region. This band is therefore assigne to the combination of C – C (phenyl in-plane) an coordinated N→O band.

The strong N – H stretching bands of all the pur triazene-1-oxides completely disappear in thei

TABLE 1—CHARACTERISATION DATA OF PHENYLMERCURY(II) COMPLEXES OF TRIAZENE-1-OXIDES

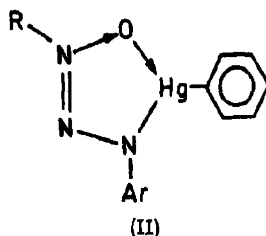
Complex	TH		Colour	m.p. °C (dec.)	%Hg	%N	%C	%H	M.W.
	R	Ar							
$[C_6H_5.Hg(T)]$	C_6H_5	$C_6H_4Cl(p)$	Greenish yellow	159-60	38.47 (38 14)	7.92 (8.00)	41.12 (41.19)	2.64 (2.67)	549 (523)
$[C_6H_5.Hg(T)]$	CH_3	$C_6H_4Cl(p)$	Colourless	169-70	43.67 (43.33)	9.23 (9.01)	33.67 (33.60)	2.55 (2.60)	452 (461)
$[C_6H_5.Hg(T)]$	C_6H_5	$C_6H_4CH_3(p)$	Yellow	151	40.13 (39.76)	8 44 (8.35)	45.22 (45.32)	3.34 (3.38)	503 (508)
$[C_6H_5.Hg(T)]$	CH_3	$C_6H_4CH_3(p)$	Colourless	128-29	45.52 (45.35)	9.49 (9.52)	37.98 (38.10)	3.36 (3.40)	443 (441)
$[C_6H_5.Hg(T)]$	C_6H_5	$C_6H_4NO_2(p)$	Yellow	195	37.91 (37.45)	10.62 (10.49)	40.34 (40.46)	2.65 (2.62)	528 (534)
$[C_6H_5.Hg(T)]$	C_6H_5	C_6H_5	Golden yellow	132-33	41.31 (40.90)	8.72 (8.59)	44.07 (44.18)	3.10 (3.07)	486 (489)

Figures in the parentheses indicate calculated values The compounds are all non-electrolytes in acetone.

phenylmercury(II) complexes, which is a strong pointer that $-N^3$ nitrogen of the ligand (I) is also coordinated to phenylmercury(II). The $\nu_{(N=N-N)}$ bands are shifted to lower frequencies due to the change in the environment of the triazene which also supports the proposed coordination through a triazene nitrogen.

Strong bands at 725-735 cm^{-1} and 438-455 cm^{-1} in these phenylmercury(II) complexes are attributed to Hg – C and Hg – O stretches[15]. A new band at 510-525 cm^{-1} in all these complexes is assigned to ν_{Hg-N} mode[16], which is absent both in the pure ligands and in phenylmercuric acetate.

In view of these observations we wish to suggest structure (II) for the phenylmercury(II) complexes of triazene-1-oxide where Hg(II) is involved in planar three-coordination. A very limited number of three-coordinate Hg(II) complexes have so far been reported in the literature[15,17].



(II)

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Complexes of 2-(o-Hydroxyphenyl)Benzthiazoline with Some Bivalent Metal Ions

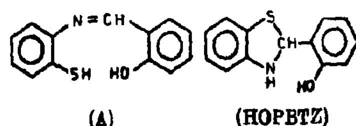
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Complexes of M^{2+} metal ion with 2-(o-hydroxyphenyl)benzthiazoline (HOPBTZ) of formula $M(OPBTZ)_2$, ($M=Mn^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} or Pd^{2+}) have been prepared and characterised from the studies of magnetic susceptibility, uv and ir spectral measurements.

THE condensation product of *o*-aminobenzthiol with salicylaldehyde is not a stable Schiff base (A) as claimed by Dubey *et al*[1] rather it undergoes cyclization reaction forming 2-(*o*-hydroxyphenyl)benzthiazoline (HOPBTZ) in good yield[2,3].



We are reporting here the preparation and characterisation of neutral inner chelates of Zn(II), Cd(II), Cu(II), Mn(II), Ni(II) and Pd(II) with HOPBTZ.

Experimental

The ligand was prepared by reported method[4]. It was used immediately after recrystallisation from ethanol.

Preparation of complexes ·

$M(OPBTZ)_2$ ($M=Zn^{2+}, Ni^{2+}$ or Cd^{2+}): An ethanolic solution of hydrated metal chloride (0.005 mol) was added to the ligand (0.01 mol) dissolved in hot ethanol (50-60 ml). From the resulting solution a small amount of impure product separated. The impure product was removed by filtration and the filtrate was made alkaline by adding excess of dilute ammonia when flocculent neutral complexes separated. The product was filtered, washed with dilute ammonia and dried *in vacuo* over $CaCl_2$.

$M(OPBTZ)_2$ ($M=Mn^{2+}$, Cu^{2+} or Pd^{2+}): An aqueous ethanolic solution of metal acetate (chloride in case of Pd^{2+}) was treated with the ligand in stoichiometric proportion. While stirring, the complex separated as granular precipitate. In case of copper the complex was obtained on diluting with excess of cold water. The product was filtered, washed with aqueous ethanol and dried *in vacuo*.

The analytical results and magnetic moment values of the complexes are shown in Table 1. UV and ir spectra of the complexes were recorded as reported earlier[4].

TABLE 1

Complex	Colour	%Metal Found (Calcd.)	%Nitrogen Found (Calcd.)	μ_{eff} B.M. (at 304°K)	Absorption band in ethanol (cm^{-1})
$Cu(OPBTZ)_2$	Dark green	12.03 (12.21)	5.42 (5.39)	1.88	25640 14290-13330
$Ni(OPBTZ)_2$	Orange yellow	11.50 (11.39)	5.32 (5.44)	Dia.	23890 21740(ϵ_{max}-68)
$Pd(OPBTZ)_2$	Yellow	19.01 (18.86)	4.98 (4.96)	Dia.	—
$Zn(OPBTZ)_2$	Cream white	12.86 (12.49)	5.12 (5.34)	Dia.	—
$Mn(OPBTZ)_2$	Orange yellow	10.80 (10.69)	5.25 (5.46)	5.84	—
$Cd(OPBTZ)_2$	Cream yellow	19.82 (20.15)	4.81 (4.91)	Dia.	—

Results and Discussion

The analytical results of the complexes correspond with the formulae $[M(OPBTZ)_2]$ ($M=Zn^{2+}$, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} or Pd^{2+}). The complexes are fairly soluble in ethanol, methanol and benzene but those of Pd(II), Mn(II) and Cu(II) are poorly soluble in ethanol and methanol but dissolve appreciably in DMF. The DMF solution of the complexes are non-conducting indicating their non-ionic nature. Ni(II), Pd(II), Zn(II) and Cd(II) complexes are diamagnetic but Cu(II) and Mn(II) complexes are paramagnetic at room temperature. The magnetic moment value of Cu(II) complex, *ca* 1.88 B.M., is similar to magnetically dilute Cu(II) complexes[5,6] and of Mn(II) complex, *ca* 5.84 B.M., is similar to four or six coordinated high spin Mn(II) complexes[7]. The electronic absorption spectra of Mn(II), Zn(II), Pd(II) and Cd(II) complexes do not display absorption band in visible region.

The absorption spectrum of $[Ni(OPBTZ)_2]$ displays medium band at 21740 (ϵ_{max}-68) assignable to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition in planar field[8,9] and a strong absorption below 25640 cm^{-1}, probably charge transfer type. Copper(II) complex displays a broad band in the region 14290-13330 cm^{-1} and a strong absorption below 23890 cm^{-1}. The former is

assigned to $E_g \rightarrow T_{2g}$ transition and latter as charge transfer band[10].

IR spectra : The ligand displays a number of bands located at 3233 m, 3023 w, 2850, 1600 m, 1575 s, 1460 m, 1451 s, 1420 sh, 1399 m, 1352 m, 1307 m, 1263 m, 1244 s, 1225 w, 1182 s, 1148 m, 1075 s, 1024 s, 920 s, 878 m, 852 w, 753 vs, 737 m, 715 m, 637 m, 575 m, 546 m, 510 m and 458 cm^{-1} due to various modes of ir vibrations of different groups present in the ligand molecules. The absence of band near 2400-2650 cm^{-1} indicates the absence of S – H group in the ligand molecule. A medium band at 3233 cm^{-1} is assigned to ν(N – H) vibration, which is shifted to lower wave number by 80-100 cm^{-1} indicating the bonding of ligand through benzthiazoline ring N – H nitrogen[11]. A medium broad band at 2850 cm^{-1} is assigned as hydrogen bonded ν(OH) vibration, which disappears in the complexes. The disappearance of the ν(OH) band indicates the coordination of ligand through deprotonated phenolic OH. A medium band at 1352 cm^{-1} assigned as OH bending band[12] also disappears in almost all metal complexes. The (N – H) bending band of the ligand located at 1575 cm^{-1} is also shifted to lower wave number by 30-50 cm^{-1} in its metal complexes supporting the involvement of N – H nitrogen in complexes. A medium band located at 1460 cm^{-1} is assigned to ν(C – O) vibration. The ν(C – O) band shifts to higher frequencies by 40 – 60 cm^{-1} in complexes The shift of ν(C – O) band suggests the increase in bond order of phenolic (C – O) group on coordination[13,14]. Since the ligand displays a number of bands in far ir region, definite frequency of (M – O) and (M – N) stretching bands could not be assigned.

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Some Studies on Thallium Oxalates—VIII : Barium *Bis*-Oxalato Diaquo Thallate(III) Monohydrate

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When about 0.01*M* thallium(III) in 0.1*M* HNO_3 is treated with 0.1*M* oxalic acid in the presence of 0.025*M* $Ba(NO_3)_2$ and 0.1*M* HNO_3 a white crystalline compound is obtained. Chemical analysis of the compound obtained corresponds to the formula, $BaTl_2(C_2O_4)_4.5H_2O$. Thermal decomposition studies indicate the simultaneous dehydration and redox decomposition of the thallium(III) salt with the formation of an intermediate, $BaTl_2(C_2O_4)_2$ stable from 150°-290° which finally decomposes to a mixture of barium carbonate and oxides of thallium(I) and thallium(III). Infrared absorption spectra, microscopic observations and X-ray diffraction data are utilised to confirm the proposed mechanism for the thermal decomposition of the compound. Basing on these results the proposed structural formula of the complex is $Ba[Tl(C_2O_4)_2(H_2O)_2]_2.H_2O$.

CONDITIONS were established[1] for the preparation of *bis*-oxalato diaquo thallate(III) with a metal-ligand ratio of 1 : 1.5. The presence of sufficient concentration of barium ion in the potentiometric titration of thallium(III) with oxalic acid was found to alter the metal-ligand ratio from 1 . 1.5 to 1 : 2[2]. The authors' findings on the preparation and analysis of the resulting solid (obtained in the presence of Ba^{2+}), its thermal behaviour, characterisation of the compound and its intermediate products of thermal decomposition using ir absorption, X-ray diffraction and microscopic observations are presented in this article.

Experimental

The experimental details of TG, DTG and DTA measurements, ir, X-ray diffraction and microscopic observations are similar to those already reported[3].

Preparation and analysis of the compound : The complex is precipitated using the conditions ($[Ba^{2+}]=0.025$ *M*; $[HNO_3]=0.1$ *M* and $[Tl^{3+}]=0.01$ *M*) reported earlier[2]. The white crystalline solid thus obtained is separated using IG 4 sintered glass crucible, washed first with minimum quantity of wash liquid (containing 0.1 *M* nitric acid and 0.025 *M* barium nitrate) and finally with acidulated (with nitric acid) water. The compound is dried under reduced pressure over anhydrous silica gel.

The ratio of thallium and oxalate contents of the compound and of the intermediate (obtained by heating the compound at 170°) are found[4] to be 1 : 2 and 1 : 1 respectively. The ratio of barium and thallium in the intermediate and hence in the original complex is found to be 1 : 2 (by difference). The presence of carbonate in the final product is confirmed by the usual acid test. By thermal studies the original complex is found[5] to contain 5 moles of water. The chemical analysis data indicates the molecular formula of the compound to be $Ba[Tl(C_2O_4)_2]_2.5H_2O$, which is further supported by the following studies.

Thermal decomposition studies : It is evident from the pyrolysis curve (Fig. 1) that the continuous loss from 50° to 150° corresponds to the dehydration (5 moles of water) and redox decomposition of thallic oxalate to thallous oxalate (with loss of two moles of oxalate i.e. 4 moles of CO_2). In the DTG curve there are two peaks indicating the stepwise loss in weight between 50° and 150°. The first slope around 100° indicates a gradual and partial dehydration and the loss in weight corresponds to one mole of water suggesting that one mole of water to be different from the rest of the water in the compound. The sharp peak around 140° and the weight of the sample at 160° indicate a rapid decomposition of the compound at this temperature. In the DTA curve a broad endothermic peak with ΔT_{min} around 95° indicates a gradual and partial dehydration while the sharp exothermic peak with ΔT_{max} at 140° indicates a rapid decomposition presumably involving simultaneous dehydration and redox decomposition steps.

The second loss from 270° to 375° in the thermogram corresponds to the decomposition of the intermediate to give rise to a mixture of barium carbonate and thallous oxide. The gain from 375° corresponds to the partial oxidation of thallous oxide to thallic oxide which is thermally stable upto 540°. The peaks in DTG around 370° indicates a sequential loss and gain in weight. The first loss might involve the decomposition of the complex to a mixture of $BaCO_3$ and Tl_2O as the weight loss tallies for this reaction, while the immediate rise in the peak presumably indicates the subsequent partial oxidation[8] of the thallous oxide by air[6]. In DTA, a sharp exothermic peak with ΔT_{max} at 370° corresponds to the decomposition of this intermediate to a mixture of barium carbonate and thallous oxide while an exothermic

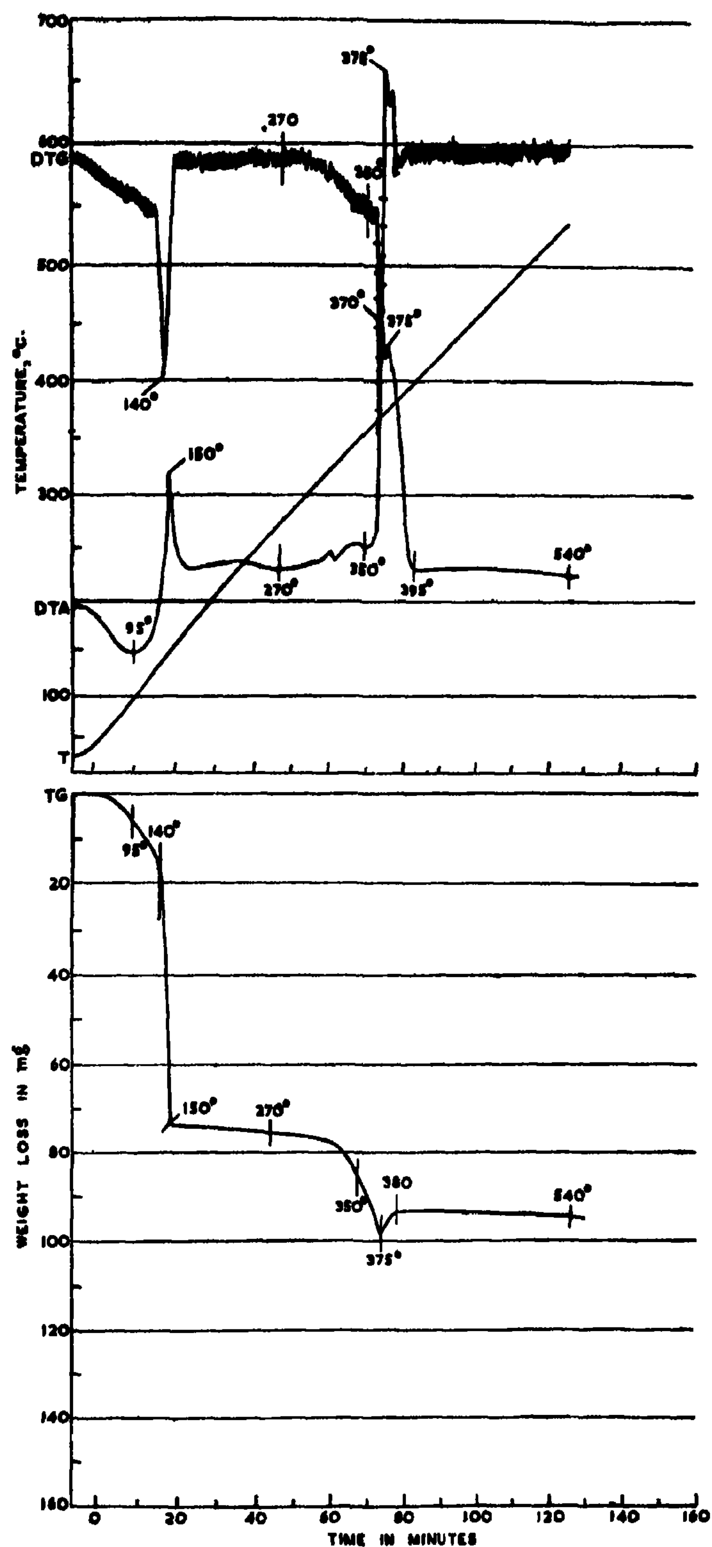
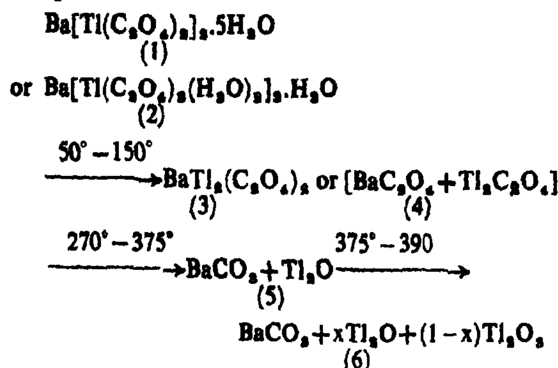


Fig. 1. T.G., D.T.G. and D.T.A. for the thermal decomposition of barium *bis*-oxalato thallate(III) pentahydrate.

shoulder with ΔT_{max} at 375° corresponds to the partial oxidation of thallium(I) to thallium(III)[6].

The above data suggest the following stepwise mechanism for the thermal decomposition of the compound.



From the thermal decomposition data alone it is not possible to ascertain the formulae of the original compound and the intermediate. Hence, the following further studies are carried out.

Infrared absorption spectral studies : The spectra of the compound and the product obtained by heating the compound upto 170° are shown in Figs. 2 and 3. The prominent characteristic peaks due to bending modes of vibration of O–C=O of thallous oxalate[8] and barium oxalate (ionic compounds) at 770 and 755 cm^{-1} have been shifted in the case of the compound to 795 and 765 cm^{-1} respectively. The shift indicates certainly some increase in the covalent character of the bond between the central metal, thallium(III), and the oxygen of the ligand, oxalate ion. The very sharp and strong peak at 795 cm^{-1} may be a combination band of carboxylate and coordinated water[6]. Hence, the molecular formula should be either (1) or (2) (a complex) and cannot be $BaC_2O_4.Tl_2(C_2O_4)_3.5H_2O$ (a double salt which is ionic).

Very broad and strong absorption peaks[7] with maxima around 3500 and 3400 cm^{-1} in Fig. 2 indicate the presence of water in the complex in any form (i. e. coordinated or lattice or both) while the absence of these peaks in Fig. 3 indicates the absence of water in the heated product (obtained by heating the complex to 170° and cooling to room temperature). This also confirms that the intermediate does not absorb moisture from atmospheric air even after cooling to room temperature. At this stage it may be worth mentioning that the heated products of other salts such as ammonium[8] and potassium[8] absorb moisture.

Microscopic observations : Barium *bis*-oxalato diaquo thallate(III) monohydrate occurs as prismatic euhedral crystals having high birefringence and showing twinkling effects. Its lower refractive index is 1.604 ± 0.002 and higher refractive index is 1.608 ± 0.002.

The microscopic observations of the crystals developed from the aqueous solution of the intermediate showed the absence of thallous oxalate[8]. This observation confirms the intermediate to be a single compound $BaTl_2(C_2O_4)_2$ and not a mixture of BaC_2O_4 and $Tl_2C_2O_4$.

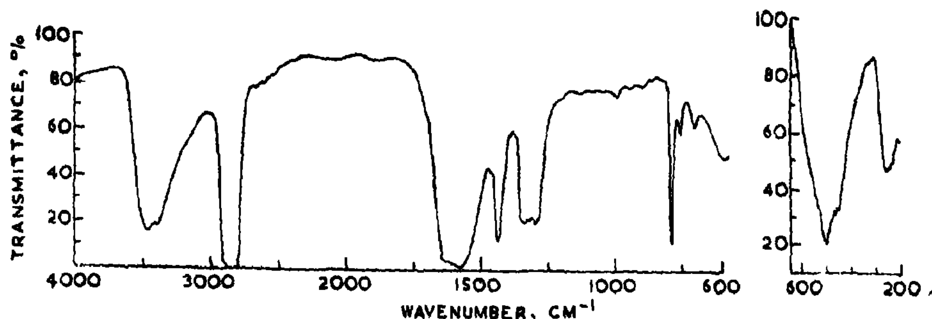


Fig. 2. Infrared spectrum of barium *bis*-oxalato thallate(III).

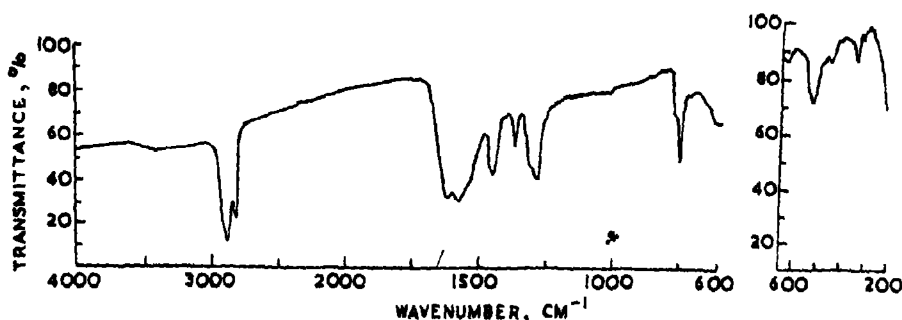


Fig. 3. Infrared spectrum of barium *bis*-oxalato thallate(III) after heating to 170°.

TABLE 1—THERMOGRAVIMETRIC DATA OF BARIUM *bis*-OXALATO DIAQUO THALLATE(III) MONOHYDRATE

Weight of the complex, mg	Step No.	Temperature °C		Loss in weight of the complex, mg		Thermal decomposition reaction proposed
		Starting	Ending	Observed	Calculated	
	I	50	150	65	64.8	$Ba[Tl(C_2O_4)_2(H_2O)_2]_2.H_2O \rightarrow BaTl_2(C_2O_4)_2$
	II	270	375	24	24 4	$BaTl_2(C_2O_4)_2 \rightarrow BaCO_3 + Tl_2O$
241	III	375	380	6 (gain)	—	$BaCO_3 + Tl_2O \rightarrow BaCO_3 + xTl_2O + (1-x)Tl_2O_3$
	overall	50	380	83	—	$Ba[Tl(C_2O_4)_2(H_2O)_2]_2.H_2O \rightarrow BaCO_3 + xTl_2O + (1-x)Tl_2O_3$

X-ray diffraction data : The X-ray diffraction data of the complex and the intermediate are compared with that of thallous oxalate[9], BaC_2O_4[10] and $BaC_2O_4.H_2O$[10]. From the comparison it is indicated that both barium oxalate and thallous oxalate are absent in the intermediate. This also confirms the intermediate to be $BaTl_2(C_2O_4)_2$. The values corresponding to the prominent reflections (6.371_x, 2.797_8 and 4.983_8) of the complex may be made use of in differentiating the barium salt from the other salts of *bis*-oxalato thallate(III)[3,8,11-15].

Conclusion : The thermal analysis results and the probable mechanism for the decomposition of the complex are summarised in Table 1.

Bis-oxalato thallate(III) is reported to be octahedral[16-18] in $H[Tl(C_2O_4)_2].3H_2O$ and $K[Tl(C_2O_4)_2].3H_2O$ on the grounds that the octahedral bonds are stronger than the tetrahedral bonds[18]. The same argument may be extended to barium *bis*-oxalato thallate(III) pentahydrate also. Moreover, the infrared spectral data confirm the presence of coordinated water in the complex suggesting it more likely to be octahedral rather than tetrahedral. The compound may therefore be formulated as :



$Ba[Tl(C_2O_4)_2(H_2O)_2]_2.H_2O$.

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Thiocyanato Substituted Nitrosyl Chromium(I) Complexes

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A new series of thiocyanato substituted nitrosyl chromium(I) having square based pyramidal and octahedral stereochemistry around the metal ion with the general formula, [CrNO(NCS)$_2$(B)] and [CrNO(NCS)$_2$(B)(py)] respectively (where B=2,2′ dipyridyl or *o*-phenanthroline) have been isolated and characterised by analysis, conductance, magnetic measurements, electron spin resonance and infrared spectral studies.

A survey of literature on neutral penta and hexa-coordinated nitrosyl chromium(I) complexes reveals that reports on such complexes are but very few[1-3]. Recently we prepared and characterised some neutral cyano substituted nitrosylchromium(I) complexes[4] and this study prompted us to characterise the thiocyanato substituted complexes. We report in this communication the preparation, properties and characterisation of some thiocyanato substituted nitrosyl chromium(I) complexes of composition, [CrNO(NCS)$_2$(B)] and [CrNO(NCS)$_2$(B)(py)] (B=2,2′ dipyridyl or *o*-phenanthroline). The complexes have been characterised by analysis, conductance, magnetic measurements, electron spin resonance and infrared spectral studies.

Experimental

All chemicals were of reagent grade. Deaerated water was used in all operations.

Preparation of diisothiocyanato dipyridylnitrosylchromium(I) [CrNO(NCS)$_2$(dipy)] : 1.0 g of K_2CrO_4 and 3.8 g of KCNS were taken in a beaker and 40 ml of water was added to dissolve the mixture. 1.0 g of $NH_2OH.HCl$ was slowly added into the solution with stirring. A vigorous reaction sets in and hence addition of $NH_2OH.HCl$ was done cautiously to control the temperature (further addition leads to the expulsion of NO). After the addition of $NH_2OH.HCl$, the reaction mixture was stirred for 1 hr and any grey colour precipitate was allowed to dissolve by adding dilute acetic acid dropwise. To the filtered green solution, 0.78 g of dipyridyl dissolved in dilute acetic acid was added. A *Khaki* colour precipitate appeared which was stirred for 1 hr at a temperature around 90° and filtered. The precipitate was washed several times with dilute acetic acid, finally washed with water, dried in air and recrystallised from methanol-petroleum ether. The yield was approximately 45%. Anal. Found : Cr, 14.6 ; C, 40.5 ; N, 19.7 ; H, 2.1 ; S, 18.1. Calcd. for [CrNO(NCS)$_2$(dipy)] ; Cr, 14.7 ; C, 40.7 ; N, 19.8 ; H, 2.2 ; S, 18.0 %.

Preparation of diisothiocyanato o-phenanthrolinenitrosylchromium(I), [CrNO(NCS)$_2$(*o*-phen)]: The corresponding *o*-phenanthroline complex was prepared analogously as described above by replacing dipyridyl with *o*-phenanthroline. The olive green recrystallised compound was analysed. Anal. Found : Cr, 13.6 ; C, 44.2 ; N, 18.3 ; H, 2.1 ; S, 16.8. Calcd. for [CrNO(NCS)$_2$(*o*-phen)] ; Cr, 13.8 ; C, 44.4 , N, 18.5 ; H, 2.1 ; S, 16.9%.

Preparation of diisothiocyanato dipyridylpyridinenitrosylchromium(I), [CrNO(NCS)$_2$ (dipy) (py)] : About 0.5 g of [CrNO(NCS)$_2$(dipy)] was dissolved in 15 ml of acetone and 1 ml of pyridine was added into it. The solution was refluxed for about 2 hr on water bath with positive pressure of the inside solvent vapour (using a pool of mercury) and the resultant solution was vacuum concentrated. The product was isolated from the solution by adding petroleum ether as yellow solid which was recrystallised from acetone-petroleum ether mixture. The yield was approximately 75%. Anal. Found ; Cr, 11.9 ; C, 47.0 ; N. 19.2 ; H, 2.9 ; S, 14.6. Calcd. for [CrNO(NCS)$_2$(dipy)(py)] ; Cr, 12.0 ; C, 47.1 ; N, 19.4 ; H, 3.0 ; S, 14.8%.

Preparation of diisothiocyanato o-phenanthrolinepyridine nitrosylchromium(I), [CrNO(NCS)$_2$ (*o*-phen)-(py)]. The *o*-phenanthroline analogue of the previous compound was prepared analogously as described earlier, by taking [CrNO(NCS)$_2$(*o*-phen)] instead of [CrNO(NCS)$_2$(dipy)]. The yellow reprecipitated compound from acetone-petroleum ether mixture was dried and analysed. Anal. Found : Cr, 11.3 ; C, 49.8 ; N, 18.2 ; H, 2.7 , S, 13.9. Calcd. for [CrNO(NCS)$_2$(*o*-phen)(py)] ; Cr, 11.4 ; C, 49.9 ; N, 18.4 ; H, 2.8 ; S, 14.0%.

Analysis : Chromium was determined as Cr_2O_3 after decomposing the complexes by heating with alkali followed by dissolving in HNO_3 and precipitating by NH_4OH. C, H and N were determined microanalytically. Sulphur was estimated as $BaSO_4$ after completely oxidising the aqueous suspension of the complexes with Br_2 water on water bath followed by acidification with dilute HCl and precipitating the sulphate with $BaCl_2$ solution.

Physical methods : Conductance was measured in analytical grade methanol using a dip type cell with the help of Philips conductivity bridge

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TABLE 1—IMPORTANT IR SPECTRAL BANDS AND ASSIGNMENTS*

Compound	$\nu(NO^+)$	$\nu(CN)$	Organic ligand	$\nu(CrN)$	$\nu(CrNO)$
$[CrNO(NCS)_2(dipy)]$	1700s	2070vs	1600m, 1576w, 1500m, 1480m, 1440s, 1372w, 1308m, 1295w, 1250w, 1210w, 1165w, 1150w, 1084w, 1070w, 1025w, 1010m, 760s, 715m, 600w.	620w	595w
$[CrNO(NCS)_2(o\text{-phen})]$	1710s	2070vs	1440w, 1415m, 1340w, 1220w, 1145w, 1105w, 880w, 845m, 765m, 740w, 710m, 695w, 650w	600w	565w
$[CrNO(NCS)_2(dipy)(py)]$	1710s	2075vs	1602m, 1575w, 1495m, 1475m, 1438w, 1310m, 1296w, 1245w, 1215w, 1170w, 1148w, 1088w, 1050w, 1020w, 1014m, 800w, 756s, 716w, 600w, 570w.	625w	592w
$[CrNO(NCS)_2(o\text{-phen})(py)]$	1710s	2080vs	1615w, 1535w, 1515w, 1451w, 1425m, 1340w, 1315w, 1220w, 1210w, 1180w, 1145w, 1107w, 1095w, 875w, 845m, 835w, 770w, 740w, 725m, 685m, 650m, 605m, 460w, 440w.	620m	570w

* Positions (cm^{-1}) and relative intensities (vs, very strong, s, strong, m, medium, w, weak).

apparatus. Infrared spectra of the complexes were recorded in KBr discs using a Perkin Elmer-621 spectrometer. Electron spin resonance spectra for the complexes were recorded with a Varian-4502 spectrometer on powdered sample and of ethanolic solution at room temperature. Magnetic susceptibilities were measured on powdered sample using a Guoy balance.

Results and Discussion

All these complexes are greenish-yellow to yellow in colour and are highly soluble in alcohol and acetone. Alcoholic or acetone solution of these complexes imparts greenish yellow colour and addition of methanolic silver nitrate does not give any immediate precipitation, but silver is deposited on standing. The molar conductivity values of these complexes are in favour of their non-electrolytic nature (Table 2).

TABLE 2—SOME PHYSICAL PROPERTIES OF THE COMPLEXES

Complex	Colour	ΛM ($\Omega^{-1}cm^2.mole^{-1}$)	μ_{eff} (B.M.)	g
$[CrNO(NCS)_2(dipy)]$	*Khaki*	15 3	1.74	—
$[CrNO(NCS)_2(o\text{-phen})]$	Olive green	12.7	1 73	1.970
$[CrNO(NCS)_2(dipy)(py)]$	Yellow	13.6	1 73	—
$[CrNO(NCS)_2(o\text{-phen})(py)]$	Yellow	12 9	1.74	1.978

The infrared spectral bands and their tentative assignments for these complexes are presented in Table 1. The appearance of a strong band in the region 1700-1710 cm^{-1} and a very strong band in the region 2070-2080 cm^{-1} are assigned to $\nu(NO^+)$ and $\nu(CN)$ respectively which are in accordance with the assignments made for the reported complexes[1,5,6]. The bands at 600-625 and 565-595 can be assigned to $\nu(Cr-N)$ and $\delta(Cr-N-O)$ respectively as reported by Miki[7] and the present author[2,3]. The coordination of organic molecules to chromium is indicated by shifts in the ligand(s) bands in the spectra of these complexes from their positions in the spectra of the free ligands. Similar shifts on complexation have been reported on several metal complexes using these ligands[8-9].

The magnetic moments of all the compounds and g values for a representative set of complexes are presented in Table 2. The magnetic moment values of 1.73 to 1 74 B. M. at 303°K for these complexes and g values of 1.970 and 1 978 for a representative set of complexes of undiluted powdered form, which are comparable to the reported compounds[2,3,5], are consistent with a low-spin d^5 configuration of Cr(I).

The analytical data and all the above results suggest the formulation of these complexes as $[CrNO(NCS)_2(B)]$ and $[CrNO(NCS)_2(B)(py)]$ (B = dipy or *o*-phen). The thiocyanate group may coordinate to the metal through either the nitrogen or the sulphur atom or both. Chromium being in the first transitional series, has been placed as class 'A' metal[10]. On coordination $\nu(CN)$ of NCS^- is lowered in N-bonded complexes than in the S-bonded complexes[11]. A comparison of the observed $\nu(CN)$ with those of the known thiocyanato complexes[6] suggest N-bonded thiocyanate group in these complexes. The use of $\nu(CS)$ to say more about the nature of coordination could not be possible here because of the presence of several other bands originating from the organic ligands in this region. However, the greater complexity in the esr spectra (ethanolic solution) suggests coordination through nitrogen.

The penta coordinated $[CrNO(NCS)_2(B)]$ complexes are assumed to be monomeric. This may be attributed to the lack of chromium to coordinate through sulphur of the thiocyanate group. This is expected having regard to the classification of chromium as a class 'A' metal[10]. The inclusion of pyridine at the sixth site forming hexacoordinated

complexes [CrNO(NCS)$_2$(B)(py)] also favours the monomeric nature. Thus, it is plausible to propose a square based pyramidal geometry to [CrNO-(NCS)$_2$(B)] on the basis of our reported result[8] and an octahedral geometry to [CrNO(NCS)$_2$(B)(py)].

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Screening of Metal Complexes for Biological Activity. Part—IV : Synthesis of Pharmacologically and Microbiologically Active Thiocyanato and Oxalato Complexes of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} with 3-Phenylaminomethylbenzoxazolinone-2

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Complexes of formula (MX2L2) where M=Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ; X=0 5 $C_2O_4^{2-}$ or SCN^- and L=3-phenylaminomethyl benzoxazolinone-2, have been prepared and characterised on the basis of analysis, conductance, magnetic moment, ir and diffuse reflectance spectral data. All the complexes were subjected to various pharmacological tests viz., toxicity, effect on CNS and CVS, antiinflammatory activity, antianaphylactic activity and diuresis. Complexes were also screened against *E. histolytica* and *S aureus* to evaluate their amoebicidal and bactericidal actions respectively. Fungitoxicity was studied against *A niger*, *A. flavus* and *F solani*. Toxicity, anti-amoebic, anti-bacterial and antifungal activities are inversely proportional to the radius of metal ion.

IN continuation of previous work on synthesis of transition metal complexes with a view to evaluate their analytical[1-3] and, pharmacological[4-6] significance we report here the coordination complexes of bivalent iron, cobalt, nickel and copper with 3-phenylaminomethylbenzoxazolinone-2. The complexes have been characterised on the basis of their analysis, magnetic susceptibility measurement, electronic and infrared spectral data. All the complexes have been subjected to various pharmacological tests viz., toxicity, effect on central nervous system (CNS), cardiovascular system (CVS), diuresis (DU), antiinflammatory activity (AIA) and anti passive cutaneous anaphylexis (PCA). In addition, amoebicidal, bactericidal and fungicidal activities of these complexes have also been evaluated.

Experimental

(a) *Chemical methods* · Iron(II), cobalt(II), nickel(II) salts and ammonium thiocyanate used were of BDH AR grade or equivalent quality. Ligand 3-phenylaminomethylbenzoxazolinone-2 (PAB) was prepared by the method of Varma and Nobles[7].

Oxalate complexes : All the oxalate complexes were prepared by refluxing appropriate metaloxalate in an ethanolic solution of the ligand in 1 : 2 for 8 hr on steambath with continued stirring. Complexes thus obtained were filtered, washed with ethanol and ether and dried in an evacuated desiccator over $CaCl_2$.

Thiocyanato-bis(*3-phenylaminomethylbenzoxazolinone-2) iron(II)* Ethanolic soln of $FeSO_4.7H_2O$ was mixed with calculated amount of NH_4SCN to get solution of $Fe(SCN)_2$ which was refluxed with 2 fold excess of ligand for 4 hr. The volume was reduced under vacuum and red crystals of desired complex were filtered and dried.

Thiocyanato-bis(*3-phenylaminomethylbenzoxazolinone-2) cobalt(II)* · On reaction with NH_4SCN (0.04 mole), the ethanolic solution of $Co(NO_3)_2.6H_2O$ (0 02 mole) yielded a dark blue solution. This solution when refluxed with ethanolic solution of ligand (PAB) yielded rose-red crystals of the desired complex The complex was filtered, washed with ethanol and ether and dried in vacuum desiccator over anhydrous $CaCl_2$.

Thiocyanato-bis (*3-phenylaminomethylbenzoxazolinone-2) nickel(II)* A cold ethanolic solution of $Ni(NO_3)_2 6H_2O$ (0.01 mole) was treated with KSCN (0.02 mole). The resulting solid KNO_3 was filtered and rejected. Treatment of the filtrate with ethanolic solution of ligand yielded violet coloured crystalline compound which was washed with ethanol followed by ether and dried under vacuum.

(b) *Pharmacological :* Details of method employed for pharmacological screening of these compelxes have been published in earlier publications[4-6].

(c) ***Microbiological :***

(i) *Amoebicidal activity :* This activity against *Entamoeba histolytica* was evaluated by the method of Das *et al*[12,13]. 0.2 ml inoculum containing about 2500 amoebae was put into cavity slide filled with 0.8 ml fresh medium having requisite drug concentration, the cavity was covered, sealed with paraffin wax and put in moist chamber at 37°. Mortality was observed after 18, 24 and 48 hr under inverted microscope. No drug was employed in control. Flagyl (1 μg/ml) was taken as reference standard. Amoebicidal end points of various complexes are listed in Table 3.

(ii) *Antibacterial activity :* Agar diffusion[14] technique was employed for assessing bactericidal activity of these complexes against *Staphylococcus aureus* (obtained from Public Analyst Laboratory, U.P., Lucknow). Sterile filter paper (Whatman No. 41) discs of 5 mm diameter saturated with soln of test compound (10 μg/ml) were kept on nutrient agar plates (1.5% w/v agar ; 0.5% w/v glucose and 2.5% w/v peptone at *p*H 6.8-7.0) after drying up the solvent. The plates were incubated at 37° for 24 hr and zones of inhibition based upon zone size (– = no inhibition, + = zone size 6.8 mm, ++ = zone size 8-12 mm, +++ = zone size 12-20 mm, ++++ = zone size $>$ 20 mm) around the disc were measured. Observations were taken as mean of duplicate experiments and bio-assay data are recorded in Table 3.

(iii) *Antifungal activity :* Fungitoxicity was evaluated against *Aspergillus niger*, *Aspergillus flavus* and *Fusarium solani* by agar plate technique[15] at three concentrations viz, 1 : 1000, 1 : 10000 and 1 : 100000. Every experiment was performed in triplicate and the average percentage inhibition was calculated. The results of fungitoxicity are tabulated in Table 3

Results and Discussion

On the basis of analytical data (Table 1) complexes have been formulated as MX_2L_2 where M = Fe(II), Co(II) or Ni(II) ; X = 0.5 $C_2O_4^{2-}$ or SCN^- ; L = 3-phenylaminomethylbenzoxazolinone-2. The molar conductances of all the complexes are less than 1.0 ohm^{-1}cm^{-2}mole^{-1} indicating that they are non-electrolytes.

A considerable negative shift in the NH stretching frequency in the complexes as compared to the ligand (at 3375 cm^{-1}) indicates the coordination of ligand through nitrogen. It has been observed that in all thiocyanate complexes C=O frequency of ligand suffered a negative shift, which indicates the involvement of ketonic oxygen in complexation. The C=O frequency of ligand interferes with the ir absorption bands of oxalate ; so it was not possible to identify ligands C=O frequency separately in these complexes.

The important infrared assignments in the oxalate complexes are of carboxylate ion. It gives two absorption bands of high intensity at 1670 and 1650 cm^{-1} which are associated with asymmetric C=O stretchings and one weak symmetric band at 1400 cm^{-1}. On coordination, asymmetric bands undergo positive shift while symmetric band is shifted to lower frequency side. The same has been found true in all oxalate complexes.

The thiocyanate complexes show bands at 805 cm^{-1} and 482 cm^{-1}, the regions of νC–S and δ NCS vibrations respectively. A band around 800 cm^{-1} in thiocyanate complexes can be assigned to the νC–S stretching mode of N-bonded thiocyanate[9].

Electronic and magnetic data :

Iron(2+) complexes : A shoulder at 370 nm in the spectrum of iron(II) complexes is attributed to $n \rightarrow \pi^*$ transition. The band at 555 nm with a shoulder around 495 nm in assigned to $T_{2g} \rightarrow \pi^*$ transition which is responsible for intense colour of iron(24) complexes. D_q value of about 924 cm^{-1} calculated from the maximum of the major (d – d) band suggests octahedral structures for these complexes.

Cobalt(2+) complexes : Bands at 1050 and 482 nm are assigned to the transitions $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ respectively. The energy of $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ transition has been calculated to be 22886 cm^{-1} (441 nm)[10]. The spectrochemical parameters of this complex, Dq = 838.28 cm^{-1}, β = 0.78, $B' = 873\text{-}2^{-cm^{-1}}$ and magnetic moment of 4.97 B.M. confirm its octahedral structure.

Nickel(2+) complexes : The electronic spectral bands at 30310 cm^{-1}, 17850 cm^{-1} and 10750 cm^{-1} are due to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ transitions. All these transitions are spin allowed transitions and are designated as V_3, V_2 and V_1 respectively. The ratio of V_2/V_1 (17850/10750) comes out to be 1.66 which suggests octahedral geometry to these complexes. Values of various ligand field parameters viz. Dq (1075 cm^{-1}), B′ (1060 cm^{-1}) and β (0.98) further substantiate the above conclusion. The magnetic moments of 3.10 and 3.25 B.M. for both the complexes of nickel also confirm the assigned geometry.

LD_{50} (the measure of toxicity) values of the complexes indicate that toxicity decreases with increasing size of the metal ion i.e. iron(2+) complexes are least toxic. In order to evaluate the effects on CNS, the compounds (at 1/5 LD_{50} dose) were administered intraperitoneally to groups of 5 albino mice and they were continuously observed for 2 hr and then at two hourly intervals for the next 6 hr. All complexes stimulated CNS as a result of which spontaneous motor activity (SMA) and reactivity increased. None of the iron complexes showed any toxic effect whereas other complexes of this series exhibited a number of toxic effects e.g. ataxia, tremor piloerection and dragging in increasing order Fe $<$ Co $<$ Ni $<$ Cu.

TABLE 1—MAGNETIC AND SPECTRAL DATA*

Compound	Colour	μ_{eff} (B.M.)	IR spectral bands (cm^{-1})				Diffuse reflectance bands λ_{max} (nm)
			NH	MN	MO	OS	
$Fe(PAB)_2(C_2O_4)$	Dark red	5.60	3280s	233m	388m	—	240, 280, 370, 494, 555, 600, 950, 1180
$Fe(PAB)_2(SCN)_2$	Dark red	5.50	3260s	229m	350m	790s	250, 295, 370, 495, 555, 960, 1240
$Co(PAB)_2(C_2O_4)$	Pink	4.97	3278s	512m	460m, 430m	—	230, 275, 305, 482, 572, 620, 1050, 1391
$Co(PAB)_2(SCN)_2$	Rose red	5.06	3260s	500m	460m, 438m	805s	245, 295, 330, 482, 618, 1050, 1220, 1387
$Ni(PAB)_2(C_2O_4)$	Green	3.25	3296s	416m	365m	—	220, 245, 278, 330, 360, 560, 655, 928, 1350
$Ni(PAB)_2(SCN)_2$	Violet	3.10	3265s	482m	350m	800s	230, 245, 330, 390, 560, 660, 930, 1300

Note—Values observed for C, H and N are in good agreement with calculated values
* For chemistry of Cu^{2+} complexes see reference No. 3.

TABLE 2—RESULTS OF PHARMACOLOGICAL SCREENING

Sl. No.	Compound	Approximate LD_{50} mg/kg i.p. (mice)	Effect on CNS (mice) at 1/5 LD_{50}	Effect on CVS (cat) at 2.5 mg/kg iv, mm Hg/minutes	A.I.A (mice) % inhibition at 1/5 LD_{50} (oral)	Anti-PCA (mice) % inhibition at 1/5 LD_{50} (oral)	Diuresis (Rat) at 1/4 LD_{50}
1.	$Fe(PAB)_2(C_2O_4)$	800	Increased SMA, reactivity and resp.	15/25	—	55	30
2.	$Fe(PAB)_2(SCN)_2$	681	—do—	2/30	34	58	30
3.	$Co(PAB)_2(C_2O_4)$	480	Increased SMA, reactivity and resp. straubtail	35/30	20	45	14
4	$Co(PAB)_2(SCN)_2$	350	Increased SMA, reactivity and resp. ataxia	35/40	18	45	12
5.	$Ni(PAB)_2(C_2O_4)$	200	Increased SMA, reactivity, ataxia, tremor and biloerection	40/30	—	60	—
6	$Ni(PAB)_2(SCN)_2$	150	—do—	50/30	—	66	—
7.	$Cu(PAB)_2(C_2O_4)$	75	Increased SMA followed by sudden decrease in SMA and resp. dragging piloerection	50/30	10	70	—
8.	$Cu(PAB)_2(SCN)_2$	75	—do—	56/45	8	78	—
9.	PAB	681	—	—	16	30	23

TABLE 3—RESULTS OF MICROBIOLOGICAL SCREENING

Sl. No.	Compound	Amoebicidal end-point against *E. histolytica* (μg/ml)	Antibacterial activity (*S. aureus*)	Antifungal activity, average % inhibition after 7 days			
				Conc	*A. niger*	*A. flavus*	*F. solani*
1.	$Fe(PAB)_2C_2O_4$	Not active	–	1 : 1000	38 0	46.7	45.0
				1 : 10000	30.6	30.5	32.0
				1 : 100000	20.0	15.0	28.4
2.	$Fe(PAB)_2(SCN)_2$	500	–	1 : 1000	35.2	38.0	36.8
				1 : 10000	28.0	26.5	28.5
				1 : 100000	15 6	15.0	16.0
3.	$Co(PAB)_2C_2O_4$	Not active	–	1 . 1000	48 5	50.0	48.5
				1 · 10000	32.0	48.6	35.2
				1 : 100000	28.5	30.5	24.8
4.	$Co(PAB)_2(SCN)_2$	250	++	1 : 1000	45.0	47.2	42.8
				1 · 10000	32.6	35 0	36.7
				1 : 100000	25.0	26.5	25.0
5.	$Ni(PAB)_2C_2O_4$	500	++	1 : 1000	74.0	72 6	70.8
				1 : 10000	68.5	65.0	65.6
				1 : 100000	56.5	58.0	56.0
6.	$Ni(PAB)_2(SCN)_2$	125	++++	1 : 1000	68.7	60 5	60.8
				1 · 10000	52.5	50.0	52.8
				1 : 100000	45.0	30.8	40.6
7.	$Cu(PAB)_2C_2O_4$	250	+++	1 : 1000	90.0	88.0	75.0
				1 : 10000	82.8	76.0	70.2
				1 : 100000	70.6	60.0	56.3
8.	$Cu(PAB)_2(SCN)_2$	62.5	++++	1 : 1000	80.6	70.8	70.0
				1 : 10000	68.0	58.6	60.6
				1 : 100000	56.2	45.0	48.0
9.	PAB	Not active	++	1 : 1000	32.6	28.5	37.6
				1 : 10000	27.8	12.0	20.5
				1 : 100000	15.0	5.0	12.8

These toxic effects further confirm the above view of increasing toxicity with decrease in metal ion size. However, in both the copper complexes stimulation of CNS was followed by depression (i.e. decreased SMA and reactivity) and it was due to super toxicity of copper complexes ($LD_{50}=75$ mg/kg). The increased rate of respiration was due to direct stimulation of respiratory centre and dilation of bronchioles.

All the complexes produced hypotension ranging from 15-56 mm of mercury for 25-45 min. These results as well as results of our earlier investigations[4,6] reveal that metallic part of the complexes is responsible for hypotension and in fact all metal complexes produced hypotension independent of coordination number and geometry. The degree and duration of hypotension have been found to be increased with decreasing size of the metal cation and actually all the copper complexes of this series produced significant hypotension, for more than half an hour. However, the ligand (PAB), when given alone did not show any sign of activity on CNS or CVS. Some of the complexes and ligand itself exhibited weak anti-inflammatory activity and diuresis.

All these complexes, when subjected to anti-anaphylactic testing produced significant inhibition. It has also been noticed that all the complexes exhibited greater inhibition as compared to the ligand. $Cu(PAB)_2(SCN)_2$ was found to be most active against passive cutaneous anaphylaxis followed by $Cu(PAB)_2C_2O_4$ and merits detailed pharmacological, biochemical and histopathological investigations. Anti-anaphylactic activity of the complexes may be either due to their preventive action on the release of histamine from the site of intradermal injection or by antagonising the action of the released histamine on the capillaries of the affected areas[8].

Fe(2+) and Co(2+) oxalate complexes of PAB are inactive against *E. histolytica* whereas Ni(2+) and Cu(2+) oxalate complexes are active only at higher concentrations. On the other hand all thiocyanate complexes are active and activity increases in the order Fe < Co < Ni < Cu. These results indicate that not only the cation but also the anion is equally responsible for the amoebicidal activity. If we consider oxalate or thiocyanate complexes separately it becomes clear that amoebicidal activity increases as the radius of the metal ion decreases. Further, the activity is potentiated if oxalate is replaced by thiocyanate. These two effects when combined together, produced most active complex $[Cu(PAB)_2(SCN)_2]$ of this series. However, PAB itself was found to be completely inactive against *E. histolytica*, which clearly indicates that coordination complexes may have more pronounced destructive effect on microorganism than their parent constituents.

First three complexes of Table 3 do not exert any destructive action against *S. aureus*, whereas compounds No. 4 and 5 rendered weak inhibition similar to PAB. However, compounds No. 6 and 8 produced significant inhibition followed by compound No. 7. These results confirm the views of Weinberg[16].

Similar to the findings of Srivastava[17] we observed here that fungitoxicity increases with decreasing radius of the metal ion and in fact copper complexes of this series exhibited pronounced antifungal activity against *A. niger*, *A. flavus* and *F. solani*. We also noticed that the complexes are more fungitoxic than ligand itself.

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Acid Dissociation Constants in Ethanol Water Mixture : Some Hydroxy Coumarins

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The pK_a values of 3-hydroxycoumarin, 4-hydroxycoumarin and 7-hydroxycoumarin in ethanol+water mixtures in the 25-90% (by volume) ethanol composition range have been determined pH-metrically using a combination of glass and calomel electrode system, at 25, 35 and 45°. The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ have also been evaluated. Increase in the concentration of water from 25 to 90% by volume, and temperature results in the decrease of pK_a for all three coumarins.

ACID dissociation constants in mixtures of solvents have been determined for a large number of hydroxyl compounds by Parsons and Rochester[1], Bates, Paabo and Robinson[2] and Jagaria and Haldar[3]. The present paper reports an investigation aimed at gaining information about the specific effects of the position of the hydroxyl group and the variation of solvent composition and temperature on the pK_a values of three different monohydroxycoumarins in ethanol + water mixture.

Experimental

The coumarins were synthesised by the reported methods, (3-hydroxycoumarin, Heilbron and Hill[4] ; 4-hydroxycoumarin, Bose and Shah[5] and 7-hydroxycoumarin, Bridge and Crocker[6]). All other reagents used were of AnalaR grade.

The samples were crystallised 3-4 times before use. The following stock solutions were prepared :

0.01M solution of each coumarin (in ethanol),
2.0M solution of sodium perchlorate (in water),
0.02M solution of perchloric acid (in water) and
0.05M solution of tetramethyl ammonium hydroxide (TMAH) (in 50% v/v ethanol)

The titrations were performed on a Beckman-Expandomatic, SS-2, pH-meter (0-14 range) fitted with a glass electrode and a calomel electrode. Temperature was maintained constant with the help of a U-10 Ultrathermostat. For each coumarin at each composition of ethanol + water mixture two titrations were carried out, the first of acid blank containing water, $HClO_4$ and $NaClO_4$ and the second of ligand blank containing water, $HClO_4$, $NaClO_4$ and coumarin and each was performed at three different temperatures (25, 35 and 45°). Titrations at different ionic strength showed no significant change in pK_a values. The volumes of various solvents added were in such amounts that the final concentration in the solution was 0.0025M with respect to coumarin, 0.001 M with respect to $HClO_4$ and 0.1 M with respect to $NaClO_4$. The final volume was 20.0 ml in each case. The titration vessel, covered with a card board with four holes, was kept in a thermostat, maintained at constant temperature. Glass and calomel electrodes were introduced through two holes. The third hole was used for a stirrer. The tip of the burette provided with a jet just closed the fourth hole. Titrations were performed for all coumarins in 25-90% (v/v) ethanol + water mixture and at different temperatures against standard 0.05 M TMAH solution. The latter solution was prepared in water for convenience. The ionic strength was kept constant in all the cases (μ=0.1 M $NaClO_4$). Results of titrations of coumarins in different ethanol + water mixtures and temperatures are summarised in Table 1 after making correction for non-aqueous medium[7].

TABLE 1—pK_a VALUES FOR THREE HYDROXYCOUMARINS IN ETHANOL WATER MIXTURES AT DIFFERENT TEMPERATURES (IONIC STRENGTH μ=0.1 M $NaClO_4$)

%(ethanol)	7-HC			3-HC			4-HC		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
25	7.86	7.76	7.66	7.16	7.06	6.96	4.36	4.26	4.21
30	8.05	7.95	7.80	7.35	7.15	7.00	4.65	4.40	4.25
40	8.22	8.12	8.01	7.52	7.32	7.12	4.91	4.62	4.47
50	8.32	8.17	8.07	7.57	7.47	7.20	4.97	4.97	4.67
60	8.39	8.19	8.09	7.59	7.49	7.34	5.04	4.99	4.89
70	8.42	8.22	8.12	7.72	7.57	7.42	5.12	5.11	5.07
80	8.57	8.42	8.32	7.77	7.67	7.47	5.34	5.27	5.02
90	8.78	8.58	8.43	7.88	7.78	7.63	5.48	5.38	5.33

Results and Discussion

At any given pH, the volumes of alkali used in the titration of strong acid ($HClO_4$) and strong acid plus coumarin have been determined from the titration curves. From the titrations performed, $\bar{n}_H$ values have been determined by the following equation used by Bjerrum, modified by Irving and Rossotti (1954)

$$\bar{n}_H = Y + \frac{(v' - v'')(N_2 + E°)}{(v° + v' + v'')T_L^°} \quad (1)$$

where Y = number of dissociable protons (for monohydroxycoumarins used Y = 1), v′ and v″ are the volumes of base (TMAH) of N_2 molarity added to a strong acid solution (acid blank) and to strong acid and coumarin solution respectively at a given pH, v^0 = total volume of solution and E^0 and T_L^0 are the concentrations of strong acid and coumarin respectively. When the concentration of undissociated coumarin is negligible compared to that of dissociated coumarin, pK_a value is given by

$$pK_a = pH + \log \frac{\bar{n}_H}{1-\bar{n}_H} \quad \dots \quad (2)$$

The pK_a values were obtained from the intercepts of the plots of log $\bar{n}_H/(1-\bar{n}_H)$ vs pH. The pK_a values for all coumarins in different compositions of ethanol + water mixture are recorded in Table 1.

The variation of pK_a with concentration of ethanol in the solvents mixture suggests that the acid dissociation constants (K_a) decrease with the increase in % ethanol in the mixture. This is in agreement with the expectation that the *ionisation* of the acid should decrease with the decrease in the dielectric constant of the solvent, as observed with other acids. A least squares fit analysis indicates the following linear relationships between the experimentally determined pK_a values and % ethanol.

3-hydroxycoumarin : pK_a = 0.0097 (% ethanol) + 6.8843, Correlation coeff. = 0.9657.

4-hydroxycoumarin : pK_a = 0.0169 (% ethanol) + 3.9350, Correlation coeff. = 0.9759.

7-hydroxycoumarin . pK_a = 0.0103 (% ethanol) + 7.6020, Correlation coeff. = 0.9545.

The temperature effect on pK_a values reveals that as the temperature increases, pK_a values decrease which is in agreement with the conclusion reached by Pitzer[8]. The thermodynamic parameters ΔG°, ΔH° and ΔS°[9] have been calculated at 25° and reported in Table 2.

TABLE 2—THERMODYNAMIC PARAMETERS FOR THREE HYDROXYCOUMARINS AT 25°

Coumarin	ΔG° KJ/mole	ΔH° KJ/mole	ΔS° J/deg/mole
7-HC	47.49	23.65	−80 0
3-HC	43.21	27.35	−53.2
4-HC	28.37	23.72	+ 1.17

Conclusion : We have made an attempt to ascertain the effect of variation of the concentration of water in water-ethanol mixture on the acid dissociation constants (K_a) of coumarins. The trends of change of pK_a values with change in water concentration in the mixtures have been found to be the same as expected from the relation of acid dissociation constant with the change in dielectric constant of the medium.

Acknowledgement

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Oxidation of Methyl Group : Kinetics of Cerium(IV) Oxidation of 2-Methyl Benzthiazole, Benzoxazole and Benzimidazole in Acetic-Perchloric Acid Mixture

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Ceric ion oxidation of 2-methyl benzthiazole, benzoxazole and benzimidazole has been examined at [$HClO_4$]=0.5*M*–2.0*M* following the disappearance of cerium titrimetrically. The rates are consistent with a mechanism involving the rapid formation of a complex which disproportionates to form the products. The rate increases with increase of [$HClO_4$] and ionic strength indicating a positive salt effect. Evidence for complex formation is obtained from Michaelis Menten reciprocal plots. The activation parameters are compared.

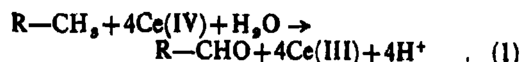
THE kinetics and mechanism of oxidation of organic compounds by Ce(IV) have received considerable attention during the past few years[1,2]. Although a large number of organic compounds have been studied, the kinetics of oxidation of methyl groups in the heterocyclic compounds have not been studied extensively so far. In a short communication on the oxidation of *alpha* picoline by Ce(IV)[3], we reported that the oxidation proceeded through a free radical mechanism and the product of oxidation was found to be an aldehyde. In this paper we report the results on the kinetics of oxidation of 2-methyl benzthiazole, benzoxazole and benzimidazole by Ce(IV) in acetic-perchloric acid medium in order to investigate the effect of hetero atoms on the kinetics.

Experimental

2-Methyl benzthiazole and 2-methyl benzoxazole (Riedel) were triple vacuum distilled before use. 2-Methyl benzimidazole was recrystallised from 50% alcohol-water. All other chemicals were of BDH (AnalaR) quality. A stock solution of Ce(IV) was prepared by dissolving ceric ammonium nitrate in 4.0 *M* perchloric acid and standardised against ferrous ammonium sulphate using ferroin as indicator. 30% aqueous solution of acetic acid was used as the medium for the reactions, since above compounds are insoluble in aqueous phase.

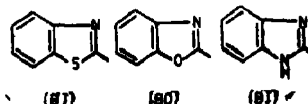
The rate measurements and the calculation of the rate constants were made according to our previous conditions[3].

Stoichiometry and product analysis: The reaction mixtures containing excess of Ce(IV) were left over night in a thermostated bath and the unreacted Ce(IV) in the reaction mixtures was determined in the usual method. It was found that 4 moles of Ce(IV) are required for each mole of the substrate oxidised and the stoichiometry may be presented as follows :



$$R{-}CH_3 + 4Ce(IV) + H_2O \rightarrow R{-}CHO + 4Ce(III) + 4H^+ \quad (1)$$

R represents benzthiazole (BT), benzoxazole (BO) and benzimidazole (BI).



The reaction products were identified as follows :

Aliquot (2 ml) of the reaction mixture was pipetted into 50 ml of *2 N* hydrochloric acid saturated at 0° with 2,4-dinitrophenyl hydrazine. Additional 10 ml of hydrochloric acid was added to ensure the solubility of hydrazine. After 30 to 60 min at 0 the 2, 4-dinitrophenyl hydrazones of the corresponding aldehydes were collected.

The products were isolated and characterised by the usual methods. The products of the oxidation were found to be the corresponding 2-aldehydes confirmed by monitoring the reaction mixture in glc and comparing the retention time with the authentic samples. Further, the formation of the products, i.e., the corresponding aldehydes were confirmed by the ir spectra.

Results and Discussion

The reactions were found to be first order with respect to Ce(IV) in the range 0.0075-0.075 *M* as

* To whom all correspondences may be made.

evidenced by the linearity of the plots of log [(Ce(IV)] vs time upto 75% of the reaction. However, it was noticed that at constant [Ce(IV)] the order with respect to the substrates is not simple and the slopes of the plots of log k vs log [sub] are not strictly unity.

Further, at constant ionic strength, the plots of $1/k_{obs}$ against 1/[Substrate] (Fig. 1) were linear making reasonable intercepts on $1/k_{obs}$ axis, thus satisfying Michaelis-Menten reciprocal relationship[4]. Hence, initial complex formation is indicated in all the cases.

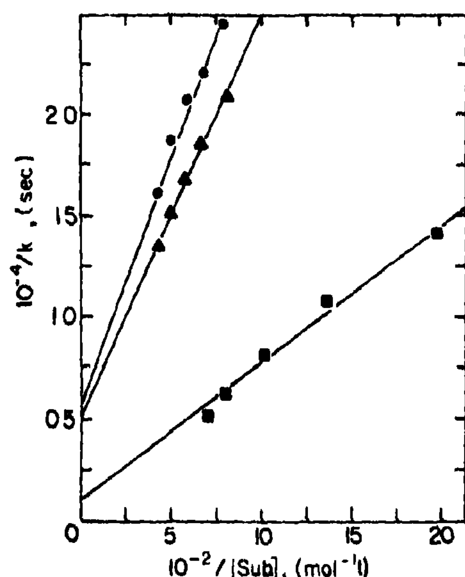


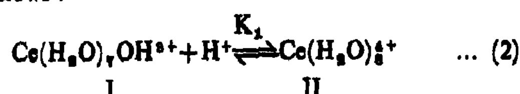
Fig. 1. Michaelis-Menten plot [Ce(IV)] = 12.5×10^{-3} M, HOAC = 30% (v/v).
(●) Benzimidazole 40°, [$HClO_4$] = 1.25 M, μ = 1.5 M
(▲) Benzthiazole 40°, [$HClO_4$] = 1.35 M, μ = 1.5 M,
(■) Benzoxazole 30°, [$HClO_4$] = 0.5 M, μ = 0.75 M.

The effect of bisulphate ion on the rate was investigated in perchloric acid solutions. There would be a slight tendency of bisulphate and H^+ to associate forming H_2SO_4. Bisulphate ions retarded the rates considerably, indicating that the bisulphate complexes of Ce(IV) are less reactive species for the oxidation. The rate of the reaction increased with increasing ionic strength, indicating a positive salt effect. Moreover, the rate of oxidation increased with [$HClO_4$].

The effect of varying solvent composition on the rate of oxidation has been studied. The rate of the reaction increased with increase in proportion of acetic acid in the reaction mixture. This dependence of rate on the solvent composition may be explained by the approaches of Ingold[5], Laidler and Eyring[6] and Amis[7]. The reaction can be classified as an ion dipole reaction, the positive species being the ionic oxidant. It is also seen that plots of log k vs 1/D give linear relationship showing that one of the reactants is an ionic one. Positive slopes of the lines give indication of charge, since according to Amis, in an ion dipole reaction involving positive ionic reactant, the rate would decrease with increase of dielectric constant of the medium.

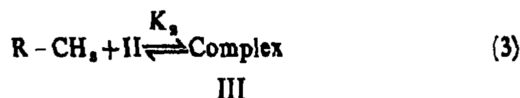
Mechanism of the reaction : Careful examination of the results indicates that the oxidation of 2-methyl heterocyclic compounds proceeds through a free radical intermediate. Evidence for the free radical intermediate is provided by the induced polymerization of acrylonitrile.

Depending on the concentration of perchloric acid, ceric ion may be present in this medium[10] as $Ce(H_2O)_8^{4+}$ and $Ce(OH)(H_2O)_7^{3+}$. Monomeric, dimeric and trimeric aceto-cerium(IV) complexes were also detected spectrophotometrically[8] in acetic acid-perchloric acid systems. Since the predominant species is monomeric in perchloric acid range 0.2-2.0 M[8], the equilibrium can be written as follows :

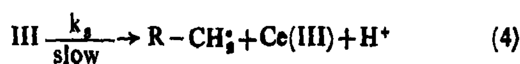


$$\underset{\text{I}}{Ce(H_2O)_7OH^{3+}} + H^+ \overset{K_1}{\rightleftharpoons} \underset{\text{II}}{Ce(H_2O)_8^{4+}} \quad \ldots (2)$$

The rate of oxidation increases with increasing [H^+] and so the unhydrolysed species (II) would be the active one. The species (II) can react with the substrate to form the complex III. This in a slow step, generates free radical which in subsequent stages of reaction with Ce(IV), is converted to the aldehyde. The reaction scheme can be represented as in eqns. (3)-(8).



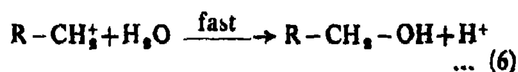
$$R-CH_3 + II \overset{K_2}{\rightleftharpoons} \underset{\text{III}}{\text{Complex}} \quad (3)$$



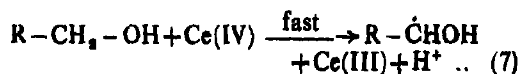
$$III \xrightarrow[\text{slow}]{k_3} R-\dot{C}H_2 + Ce(III) + H^+ \quad (4)$$



$$R-\dot{C}H_2 + Ce(IV) \xrightarrow{\text{fast}} R-CH_2^+ + Ce(III) \quad \ldots (5)$$



$$R-CH_2^+ + H_2O \xrightarrow{\text{fast}} R-CH_2-OH + H^+ \quad \ldots (6)$$



$$R-CH_2-OH + Ce(IV) \xrightarrow{\text{fast}} R-\dot{C}HOH + Ce(III) + H^+ \quad \ldots (7)$$



$$R-\dot{C}HOH + Ce(IV) \xrightarrow{\text{fast}} R-CHO + Ce(III) + H^+ \quad \ldots (8)$$

The rate expression from equations (3)-(8) is (9), from which equation (10) follows, where k_{obs} is the observed rate constant.

$$\frac{-d[Ce(IV)]}{dt} = k_{obs}\,[Ce(IV)] = \frac{K_1K_2k_3[Ce(IV)][R-CH_3][H^+]}{K_1K_2[H^+][R-CH_3] + K_1[H^+] + 1} \quad \ldots (9)$$

$$\frac{1}{k_{obs}} = \frac{1}{k_3} + \frac{1}{[R-CH_3]}\left[\frac{1+K_1[H^+]}{K_1K_2k_3[H^+]}\right] \quad \ldots (10)$$

Accordingly at constant [H^+], plots of $1/k_{obs}$ against 1/[substrate] should be linear and it is observed to be so (Fig. 1). The values of k_2 are found to be 8.3×10^{-4}, 2.0×10^{-4} and 1.6×10^{-4} sec^{-1} in case of 2-methyl benzoxazole, 2-methyl benzthiazole and 2-methyl benzimidazole respectively.

The results for the oxidation of different methyl substituted compounds in the temperature range 35-50° are given in Table 1. Comparing the thermodynamic parameters as evidenced from Table 2, the order of the reactivities may be presented as follows :



$$2\text{-}CH_3BO > 2\text{-}CH_3BT > 2\text{-}CH_3BI$$

The sequence of reaction can be explained if the mechanism of the reaction as suggested in equations (3) to (8) is assumed. The 2-methyl substrates combine with the active species of Ce(IV) forming a complex in a fast step. The rate limiting step is, therefore, the decomposition of the complex forming the corresponding free radical at the methyl carbon atom. So the reactivities of different 2-methyl compounds will depend on the stability of the free radical at the methyl carbon atom. In the reaction condition studied by us, the hetero atoms will very likely combine with the protons forming the corresponding protonated ions. The stability of the free radical will, therefore, depend on the nature of the protonated hetero atoms.

In case of benzimidazole, since ammonium ion is very stable, the free radical will not derive much stability from the electrons of the nitrogen atom. The reactivity of 2-methyl benzimidazole will, therefore, be expected to be the least of all.

Sulphonium ion is more stable than oxonium ion. Arguing as above, the free radical on the methyl carbon will be stabilised more in 2-methyl benzoxazole than in 2-methyl benzthiazole. The observations, therefore, correspond to the expected sequence of reactivity.

TABLE 1—EFFECT OF TEMPERATURE ON THE RATE

[Ce(IV)]=0.0125 *M*, [Substrate]=0.0125 *M*, HOAC=80% (v/v)

Temp °C	k_{obs} (sec^{-1}) × 10^5
2-Methyl benzoxazole	([$HClO_4$]=0.5 *M*, μ=0.75 *M*)
30	17.0
35	24.4
40	46.0
45	81.0
2-Methyl benzthiazole	([$HClO_4$]=1.35 *M*, μ=1.5 *M*)
35	4.0
40	5.6
45	12.3
50	21.8
2-Methyl benzimidazole	([$HClO_4$]=1.25 *M*, μ=1.5 *M*)
40	4.1
45	8.5
50	16.3

TABLE 2—THERMODYNAMIC PARAMETERS FOR Ce(IV) OXIDATIONS

	E K cals/mole	$\Delta S^{\neq}$ Cal/deg/mole
2-Methyl benzoxazole	19.8	−12.4
2-Methyl benzthiazole	22.5	− 8.07
2-Methyl benzimidazole	28.5	+ 8.3

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A Kinetic Study of Oxidation of Isobutyl Alcohol with Aqueous Iodine

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Oxidation of isobutyl alcohol with aqueous iodine has been studied at constant *p*H (9.18). The reaction is zero and first order with respect to iodine and substrate respectively. The reaction is base catalysed and is found dependent on the first power of OH^- ion concentration. The influence of various factors i.e. ionic strength, *p*H, dielectric constant, D_2O and temperature on the reaction rate have been studied and hydride abstraction mechanism has been suggested for the reaction.

OXIDATION of alcohols by halogens particularly by chlorine and bromine have been studied by various workers[1-4]. Two types of mechanism have been suggested. Ester mechanism was suggested for the reaction of isopropyl alcohol and bromine[5] or chlorine[6]. Kaplan[7] and Banerjee[8] suggested hydride abstraction mechanism for the oxidation of alcohols. The oxidation of benzhydrols by iodine in alkaline medium (non-aqueous) has been reported by Ogata and Nagura[9].

However, earlier studies were conducted mainly in the acid medium. In alkaline aqueous medium halogens are mostly converted to inert hypohalite anion[10], due to which oxidising conditions may change. In the present paper results of investigation on oxidation of isobutylalcohol with aqueous iodine in alkaline medium are reported.

Experimental

All chemicals were of reagent grade. Double distilled water was used in preparing all solutions. Stock iodine solution was prepared by dissolving iodine in aqueous solution of potassium iodide. The reactions were carried out at constant ionic strength (μ=0.2 *M*) using sodium perchlorate. Borax solution was used to maintain constant *p*H of 9.18. To avoid photochemical effects, reaction bottles, blackened from outside were used and were suspended in thermostat for at least 30 min before starting the reaction. The reaction was monitored by estimating the unreacted iodine at various intervals of time by standard hypo solution. Suitable quantity of potassium iodide was added to avoid simultaneous hydrolysis of iodine during the reaction. Kinetic measurements are reproducible within 1% error.

Product analysis : The stoichiometry shows that 1 mole of isobutyl alcohol reacts with 1 mole of iodine to give isobutyraldehyde which was identified from the reaction mixture by precipitation of its 2, 4-DNP derivative and spot test[11]. The end product was identified to be isobutyric acid.

Results and Discussion

Out of the four species I_2, HOI, H_2OI^+ and I_3^- which may be existing in the aqueous iodine solution, iodine acts as an oxidising agent[12]. In the large concentration of alcohol the order of reaction has been found to be zero as indicated by the constancy of x/t or by the linear plot of x vs t passing through origin (x is the number of moles of iodine consumed in time t). By varying the concentration of alcohol or iodine the rate was found to depend on the first power of alcohol concentration and independent of iodine concentration (Table 1).

TABLE 1—DEPENDENCE OF OXIDATION RATE ON THE CONCENTRATION OF ISOBUTYL ALCOHOL AT 35°

[KI]=0.06 *M* ; μ=0.20, *p*H=9.18

$[I_2]\times10^4$ *M*	5.0	15.0	40.0	60.00	8.0	8.0	8.0	8.0
[Alc] × *M*	0.10	0.10	0.10	0.10	0.02	0.20	0.30	0.40
$k\times10^6$ *M* sec^{-1}	2.12	2.09	2.09	2.09	0.41	4.07	6.18	8.29
$k'\times10^5$/[Alc]sec^{-1}	2.12	2.09	2.09	2.09	2.05	2.03	2.06	2.07

The plot of $1/k_{obs}$ vs 1/[ROH] at 35° is linear with no intercept on the axis. This shows the absence of a preformed complex or complex whose formation constant is too low to be kinetically determined. The reaction was found to be base catalysed. The initial rate[13] of the reaction was determined in the presence of varying concentrations of OH^- ions. Since NaOH and I_2 also react simultaneously, the initial rate for this reaction was also determined separately under similar conditions. Thus the first order rate constant with respect to OH^- ions was calculated (Table 2). The rate equation can be written as

$$\frac{-d[I_2]}{dt}=k\,[Alc]\,[OH^-]$$

*For correspondence.

TABLE 2—DEPENDENCE OF OXIDATION RATE ON THE CONCENTRATION OF OH^- IONS AT 35°

$[I_2]=0.001\ M$; $[Alc]=0.05\ M$; $[KI]=0.06\ M$, $\mu=0.2\ M$

[NaOH] M	Initial rate with alcohol $k_0'' \times 10^6$ $M\ sec^{-1}$	Initial rate without alcohol $k_0' \times 10^6$ $M\ sec^{-1}$	$(k_0''-k_0')=k_0 \times 10^6$ $M\ sec^{-1}$	$k_0 \times 10^4$ / $[OH^-]$, sec^{-1}
0.004	3.66	3.30	3.6	9 00
0.005	4.14	3.70	4.4	8.80
0.006	4.44	3.92	5.2	8.66
0.007	4.74	4.12	6.2	8.85
0.008	4.96	4.26	7.0	8.75

When the concentration of $NaClO_4$ was varied (0.05 *M* to 0.5 *M*), the rate of the reaction was found to remain almost constant indicating that either two molecules or a molecule and ion are involved in the reaction. This fact was further confirmed by studying the reaction in varying concentrations of dioxan and water (v/v). The rate was found to increase with the decrease in dielectric constant (Table 3) showing that reaction was taking place between ion and molecule[14].

TABLE 3—ISOBUTYL ALCOHOL AND AQUEOUS IODINE IN DIOXAN-WATER AT 25°

$[Alc]=0.1\ M$, $[I_2]=0.001\ M$, $[KI]=0.06\ M$, $\mu=0.2\ M$, pH=9.18

% Dioxan	0	5	10	20	30	35
Dielectric constant	78 5	74.9	71.3	62 2	53.5	48.8
$k \times 10^7$, $M\ sec^{-1}$	1.04	1.81	3.16	4 16	9 16	12.50

Effect of iodide ions : Effect of iodide ions on the reaction rate was studied by the addition of varying concentration of KI and cadmium iodide. The rate was found to decrease with the increase in the concentration of iodide ions, showing the formation of iodide ions in the reaction equilibrium.

Isotope effect : The rate k_{D_2O}/k_{H_2O} at 35° has been determined to be 1.67 indicating the possibility of deprotonation[15] of isobutyl alcohol in the rate determining step.

Effect of temperature : Activation parameters were calculated from the different values of rate constants obtained at different temperatures by usual methods (Table 4).

TABLE 4

E_a k.cal/mol	$\Delta H^{\#}$ k.cal/mol	$\Delta S^{\#}$ e.u.	$\Delta G^{\#}$ k.cal
12.55 ± 0.17	12.09 ± 0.44	-54.63 ± 0.04	$28\ 8 \pm 0.38$

Temp., °C	25	30	35	40	45
$k \times 10^6$, $M\ sec^{-1}$	1 04	1.57	2 08	3.15	4.13

For simple ion-dipole interactions, the principal contribution of $\Delta G^{\#}$ is the increase in free energy arising from the distribution of charge over a large ion X in the transition state. On such basis ion dipole reaction should be accelerated in solvents of decreasing dielectric constant (Table 3). Thus, large positive value of $\Delta G^{\#}$ is in confirmation with the nature of reaction. High negative value of entropy is due to the influence of charge in the initial state of reactants and final state of the activated complex along with induced dipole forces.

Effect of pH *change* : Borate buffers were used to study the effect of change of *p*H. The rate was found to increase with increase in *p*H value (Table 5).

TABLE 5—EFFECT OF pH VARIATION ON THE REACTION RATE AT 35°

$[I_2]=0.0008\ M$, $[Alc]=0.10\ M$, $[KI]=0.01\ M$, $\mu=0.2\ M$

pH	7.25	8.17	9 2	9.79
$k' \times 10^7$, sec^{-1}	0.92	1.48	4.89	9.8

Aqueous alcohols are found to exist in the following equilibrium :

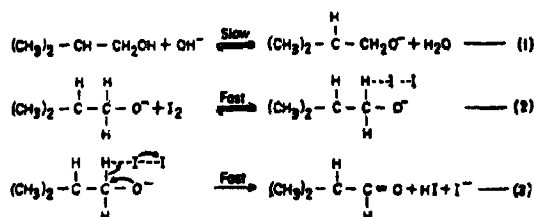


$$R-OH+H_2O \rightleftharpoons RO^- + H_3^+O$$

With the increase in *p*H, the above equilibrium shifts towards the right increasing the concentration of RO^- ions in the solution. It has been shown[3,4,16] that alkoxide ions are more easily oxidised than their molecular form. Iodine being a weaker oxidising agent than chlorine and bromine seems to have little tendency to attack molecular form which is indicated in the study of *p*H rate profile. Since the rate is found to depend on the concentration of alcohol (Table 1) and not on the iodine concentration, the increase in the rate with increase in the *p*H value may be due to the increase in the concentration of alkoxide ions.

Alkoxide ions are good hydride donor[17] as α-hydrogen on them may easily be removed due to the tendency of the negatively charged oxygen atom to form a double bond with carbon. Also the reaction of halogens with negatively charged ions are more likely than with undissociated molecules owing to the strong electron attracting character of the halogens[18].

Thus on the basis of above facts following mechanism can be proposed :



All subsequent steps leading to the formation of acid are considered to be fast. This assumption has been verified by determining the rate of oxidation of isobutyraldehyde under similar conditions of experiment which is found to be 370 times faster than the rate for oxidation by alcohol.

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Kinetics of Nickel(II) Ion and Cobalt(II) Ion Catalysed Hydroxamic Acid Formation from Formic Acid

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The Kinetics of Ni(II) ion catalysed formation of hydroxamic acid from formic acid and hydroxylamine revealed to be first order each with respect to formic acid, hydroxylamine and Ni(II) ion concentration. Cobalt(II) ion is comparable with Ni(II) ion in its catalytic efficiency, but its catalytic effect is weaker than that of the Ni(II) ion. The activation parameters have been evaluated and a probable mechanism has been suggested.

AS a special type of amide, hydroxamic acid can be formed by the reaction of hydroxylamine with carboxylic acid in neutral and acidic medium[1,2]. Working with aliphatic carboxylic acids and aliphatic amines, Morawetz and Otaki[3] were able to detect amide formation in aqueous solution, although 'activation' of an acyl group (by converting into an ester, acid anhydride, thiol ester, acyl phosphate, etc.) is usually considered to be a prerequisite to amide formation[4]. The present paper reports the kinetics of the reaction of hydroxylamine with formic acid catalysed by Ni(II) ion and Co(II) ion in aqueous solutions.

Experimental

Material and method : Ferric chloride reagent (0.15 *M*) was prepared by dissolving 40.545 g of ferric chloride hexahydrate and 50 ml conc. HCl in water to make 1 litre. All other chemicals were of reagent grade.

Kinetic measurement : The kinetics of hydroxamic acid formation was studied by preparing various sets of reaction mixture. In each case appropriate aliquots of reactant solutions were mixed in a reaction flask and *p*H of the solution was adjusted with strong NaOH or HCl solutions. Portions (3 ml) of the reaction mixture, thus prepared, were sealed in glass ampoules and placed in a thermostated water bath to initiate the reaction. Ampoules were removed at recorded time intervals and the reaction was quickly quenched by immersing the ampoules in an ice bath. One ml content of an ampoule was added to 20 ml ferric chloride reagent contained in a 25 ml volumetric flask. The absorbance due to ferric hydroxamate complex was measured at 530 nm by spectrophotometer 'Speckol'[5,6].

Results and Discussion

Ni(II) ion catalysed hydroxamic acid formation : The initial concentrations used for the study of Ni(II) ion catalysed formohydroxamic acid formation were formic acid 0.04 *M*, hydroxylamine hydrochloride 0.8 *M* and nickel chloride 0.04 *M*.

The order of reaction (n) calculated by van't Hoff differential method is found to be 1.0 with respect to formic acid (Table 1), 0.9 with respect to hydroxylamine (Table 2) and 0.75 with respect to nickel chloride (Table 3). The deviation from unity may be attributed to the complexity of the reaction.

TABLE 1—EFFECT OF VARYING FORMIC ACID CONCENTRATION ON INITIAL REACTION RATE AT 90.5°

($NiCl_2$)=0.04*M*, ($NH_2OH.HCl$)=0.8 *M*, *p*H=5.25 (measured at 27°)

(Formic Acid) *M*	Initial rate Vo ($M\ sec^{-1}$)$\times 10^{6}$	n
0.02	1.90	1.0
0.03	2.85	1.0
0.04	3.80	1.0
0.06	5.94	

TABLE 2—EFFECT OF VARYING $NH_2OH.HCl$ CONCENTRATION ON INITIAL REACTION RATE AT 90.5°

(HCOOH)=0.04 *M*, ($NiCl_2$)=0.04 *M*, *p*H=5.25 (measured at 27°)

($NH_2OH.HCl$) *M*	Initial rate Vo ($M\ sec^{-1}$)$\times 10^{6}$	n
0.4	1.90	1.00
0.6	2.85	0.91
0.8	3.80	0.89
1.0	4.63	0.90
1.2	5.46	

TABLE 3—EFFECT OF VARYING $NiCl_2$ CONCENTRATION ON INITIAL REACTION RATE AT 90.5°

(HCOOH)=0.04 *M*, ($NH_2OH.HCl$)=0.8 *M*, *p*H=5.0 (measured at 27°)

($NiCl_2$) *M*	Initial rate Vo ($M\ sec^{-1}$)$\times 10^{6}$	n
0.04	3.32	
0.06	4.51	0.75
0.08	5.32	
0.10	6.41	0.81
0.12	7.86	0.75

Assuming the rate equation $V=k'(HCOOH)_T(NH_2OH)_T$, the apparent second order rate constant

k' can be calculated from initial rate measurements. The reaction was studied at different temperatures and the various activation parameters are reported in Table 4. The rate constant expression for the reaction of hydroxylamine with formic acid in the presence of Ni(II) ion can be expressed as

$$k = 1.2 \times 10^{4} e^{-15610/RT} M^{-1}\ sec^{-1}$$

TABLE 4—VARIATION OF REACTION RATE WITH TEMPERATURE

$(NiCl_2) = 0.04\ M$; $(NH_2OH.HCl) = 0.8\ M$; $(HCOOH) = 0.04\ M$; $pH = 5.0$ (measured at 27°)

Temperature (°C)	70	75	80	85	90
$k' \times 10^{6}$ (M^{-1} sec^{-1})	0.33	0.49	0.67	0.96	1.26

Activation parameters
E_a = 16.6 ± 0.8 k cal/mole
$\Delta S^{\neq}$ = −42.1 ± 0.2 e.u.
$\Delta H^{\neq}$ = 15.9 ± 0.1 k cal/mole
A = 1.2×10^{4} sec^{-1}

The *p*H rate profile (Fig 1[A]) for Ni(II) ion catalysed hydroxamic acid formation can be calculated by the equation (1).

$$v = k'_2[HCOOH][NH_2OH][H^+] + k'[HCOOH][NH_2OH] + k_{Ni}[HCOO^-][NH_2OH][Ni^{++}] \quad (1)$$

The first term corresponds to hydrogen ion catalysis whereas the second term involves no catalyst. However, the third term corresponds to Ni(II) ion catalysed reaction of hydroxylamine with the formate ion (Fig. 1).

Fig. 1. *p*H rate profile for formohydroxamic acid formation at 90.5°.
[A]→$[HCOOH] = 0.04\ M$; $[NH_2OH.HCl] = 0.8\ M$, $[NiCl_2] = 0.04\ M$.
[B]→$[HCOOH] = 0.04\ M$; $[NH_2OH.HCl] = 0.8\ M$; $[CoCl_2] = 0.04\ M$.
[C]→$[HCOOH] = 0.04\ M$; $[NH_2OH.HCl] = 0.8\ M$.

Complexation of Ni(II) ion with hydroxylamine would decrease the electron density on the nitrogen atom of hydroxylamine, making it a poorer nucleophile. A catalytically favourable chelate complex involving formate ion may be formulated as under.

$$H-C\{O,O\}^- \cdots Ni^{2+}$$

Formation of such a complex will make carbonyl carbon atom more electron deficient and therefore make it more susceptible to a nucleophilic attack.

Based on the kinetic data, the following probable mechanism for Ni(II) ion catalysed hydroxylaminolysis of formic acid is suggested.

Scheme-I

(Uncatalysed reaction)

$$H.COOH + NH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H-C(OH)(OH)-NHOH \quad \ldots (A)$$

$$H-C(OH)(OH)-NHOH \xrightarrow{slow} HCONHOH + H_2O$$

Scheme-II

(Acid catalysed reaction)

$$HCOOH + H^+ \overset{K}{\rightleftharpoons} HCOOH_2^+$$

$$HCOOH_2^+ + NH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H-C(\overset{+}{O}H_2)(OH)-NHOH \quad \ldots (B)$$

$$\downarrow$$

$$HCONHOH + H_3^+O$$

Scheme-III

Ni(II) ion catalysed reaction

$$HCOO^- + Ni^{2+} \overset{K}{\rightleftharpoons} H-C\{O,O\}^- \cdots Ni^{2+}$$

$$\underset{(C)}{H-C\{O,O\}^- \cdots Ni^{2+}} + NH_2OH \overset{H^+}{\rightleftharpoons} \underset{(D)}{H-C(OH)(OH)-NHOH} + Ni^{2+}$$

$$(D) \rightarrow HCONHOH + H_2O$$

Cobalt(II) ion catalysed hydroxamic acid formation : The comparison of *p*H rate profile for Ni(II) ion and Co(II) ion catalysed (Fig. 1[A] and [B]) formation of hydroxamic acid reveals that Ni(II) ion is a better catalyst than Co(II) ion[7,8].

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Ion Exchange Selectivity of Monovalent Ions in Aqueous and 50% Ethanol-Water Media towards *Tris*-Trimethylene Diamine Co(III) Exchanged Amberlite-IRC-50

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The exchange isotherms of $Co(tn)_3^{3+}$ from Na-$Co(tn)_3$-IRC-50 by monovalent ions in aqueous and 50% *ethanol-water (v/v)* media are of the S-type indicative of cooperative sorption. In aqueous solution the desorption efficiency of the ions is in the order : $NH_4 > Li > Na > K > Rb > Cs$ while in 50% ethanol-water the sequence is $Na > K > Li > Rb > Cs$. The extent of release of $Co(tn)_3^{3+}$ from the resin matrix by each ion is much higher in 50% ethanol-water medium than in pure aqueous solution. It has been suggested that site binding of the ions with the resin followed by release of water molecules from the solvation shells of the participating species takes place. The plots of log(selectivity coefficient) against both the hydrated ionic radius and the reciprocal of the Debye Hückel ion-size parameter a° in aqueous medium are linear. This implies that both the parameters may be used to correlate the relative affinities of the monovalent ions for the resin surface.

STUDIES on ion exchange equilibria have revealed that the selectivity of a cation exchanger polymer is influenced by many factors such as the structure of the polymer, the nature of the functional group and the mole fraction of the exchanging cations in the polymer phase[1,2]. Thus, the affinity sequence of the alkali metal cations in their exchange reactions in aqueous solutions on crosslinked polymethacrylic acid exchangers[3,4] has been shown to be the reverse of that with polystyrene sulphonates[5,6] where the order is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. It has been suggested that in polymethacrylates specific association between the counter ions and the fixed ionic groups, i.e. site binding[4], takes place and is accompanied by the release of water molecules from the solvation shells of the participating species. With polystyrene sulphonate exchangers, however, it has been inferred that ion-water interactions[5] are of prime importance in determining the order of alkali metal cation selectivity. Recently Matsuura[7] had proposed the use of cation exchange resins loaded with $Co(NH_3)_6^{3+}$ or $Co(en)_3^{3+}$ for the continuous extraction of recoil products in Szilard-Chalmers reaction for obtaining a high yield and specific activity and found them most suitable for this method because these complex ions give rise to the bivalent cobaltous ion upon neutron irradiation[8,9]. In view of the above theoretical and practical interests, the exchange characteristics of *tris*-trimethylene diamine Co(III) i.e. $Co(tn)_3^{3+}$ from $Na-Co(tn)_3$-IRC-50 against a number of monovalent ions in aqueous and 50% aqueous-ethanolic medium have been investigated and are reported here. The experimental exchange data have also been analysed in the light of the simple electrostatic model of Pauley[10].

Materials and methods. Amberlite-IRC-50, a copolymer of methacrylic acid crosslinked with divinyl benzene and a carboxylic acid type exchanger (≈50 mesh particle sizes) was used. The exchange capacity of the H-resin was found to be 1020 meq/100 g of the dry resin (dried at 105°) and was determined by shaking the resin with a measured excess of standard NaOH solution and then back titrating the excess alkali with HCl. The H-exchanger was converted into the Na-form by adding an equivalent amount of NaOH. The experimental details for studying the exchange of $Co(tn)_3^{3+}$ onto Na-resin and its subsequent desorption by the monovalent ions are similar to those reported earlier[11]. The hydration status of H^+, Na^+ and $Co(tn)_3^{3+}$ saturated resins were determined with the help of a modified apparatus as used by Baver[12]. The intake of water per g of resinate gives an idea of the relative hydration characteristics of the solids.

Results and Discussion

The maximum uptake of $Co(tn)_3^{3+}$ onto Na-form of Amberlite IRC-50, a weak carboxylic cation exchanger, corresponds to 704 meq/100 g as against the exchange capacity of the resin which is 1020 meq/100 g. The lower value may be caused by the physical inaccessibility of some of the exchange sites of the resin to the large-sized $Co(tn)_3^{3+}$ ions. It is interesting to note from Fig. 1 that the exchange isotherms of $Co(tn)_3^{3+}$ from Na-$Co(tn)_3$-IRC-50 with the monovalent ions in aqueous and 50% aqueous ethanolic media are of the S-type in the classification of sorption isotherms of Giles *et al*[13]. Moreover, the general lyotrope series is also reversed in aqueous medium except in

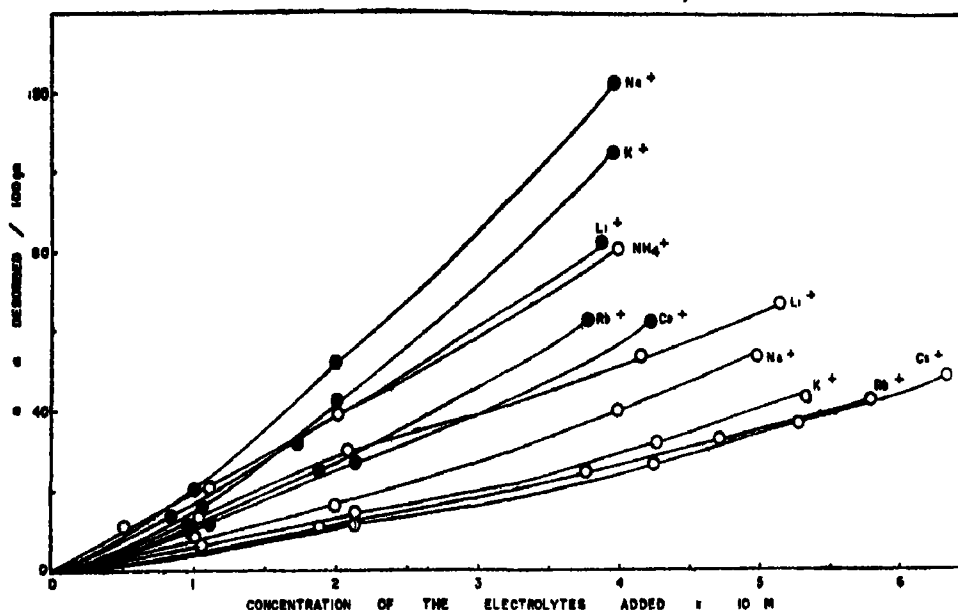


Fig. 1. Exchange isotherms of $Co(tn)_3^{3+}$ from Na-$Co(tn)_3$-IRC- 50 by monovalent ions in aqueous (O) and 50% aqueous-ethanolic medium (●).

the position of NH_4^+. The S-type of isotherms indicate cooperative adsorption i.e. adsorption occurs with increasing ease as solute concentration increases in the initial part of the isotherm, suggesting that adsorbed molecules encourage the retention of additional like-molecules. Recent theoretical treatment by Giles[18] *et al*, however, shows that this type of curve occurs when the activation energy for desorption of the solute is concentration dependent, and/or is markedly reduced by large negative contributions of the solvent or a second solute.

The intake of water by H^+, Na^+ and $Co(tn)_3^{3+}$ forms of the resin are 2.1, 3.6 and 1.78 ml per g of the resinates respectively. The data clearly show that a hydrophobic character is developed in the resin matrix when H^+ or Na^+ is replaced by $Co(tn)_3^{3+}$, while a hydrophilic character is noticed when H^+ is exchanged by Na^+. So it is very likely that due to the presence of a hydrophobic layer, ion such as Na^+ is not easily accessible to the resin surface unless a considerable amount of the initially adsorbed $Co(tn)_3^{3+}$ ions get desorbed and replaced by hydrophilic ions. As result, the amount of $Co(tn)_3^{3+}$ desorption is very small at lower concentrations of the desorbing ions. Lindenbaum and Boyd[4] obtained an increase in entropy in the exchange of Li^+ for Cs^+ in crosslinked polymethacrylate exchangers and this preference for Li^+ has been explained by assuming a specific association, i.e. site binding between Li^+ and the carboxylate group of the exchanger, with the release of water molecules. Further, dilatometric measurements[14] with linear polymethacrylate have shown that a volume increase of *ca* 3 ml per equivalent occurs in the system when tetramethylammonium counter ions are replaced by Li^+ or Na^+. If water is released in site binding, an appreciable positive contribution to ΔS° also would be expected[15]. These effects have been ascribed to a competition between water of hydration and anion for a position near a given cation and ultimately to the charge distributions, polarizabilities, and effective field strengths of the participating ions[16]. Similar assumptions may be made here to explain the cation sequence in the exchange of $Co(tn)_3^{3+}$ by the monovalent ions in the present work.

To investigate the role of ionic hydration in the exchange reactions[17], the desorption experiments have also been done in 50% ethanol-water medium (Fig. 1) at different concentrations of Li^+, Na^+, K^+, Rb^+ and Cs^+. It can be noted that with each of the desorbing electrolytes the release of $Co(tn)_3^{3+}$ from the resin matrix is much higher than in the pure aqueous medium. The order of preference for the resin is $Na^+ > K^+ > Li^+ > Rb^+ > Cs^+$, which is different as observed in pure aqueous solution. This behaviour may be attributed to the altered solvation of these ions, the resulting ionic sizes, their activities and the dielectric constant effects on coulombic interactions.

The selectivity coefficients of the exchanging ions in aqueous medium have been computed as in our previous paper[11] from the following relation,

$$K^1_{Co(tn)_3^{3+}} = \frac{[\bar{i}^{z+}]^{1/z}[Co(tn)_3^{3+}]^{1/3}}{[\overline{Co(tn)_3^{3+}}]^{1/3}[i^{z+}]^{1/z}}$$

where the bracket and the bar mean the concentrations of the ions in the solution and resin phases respectively. The distribution coefficients have

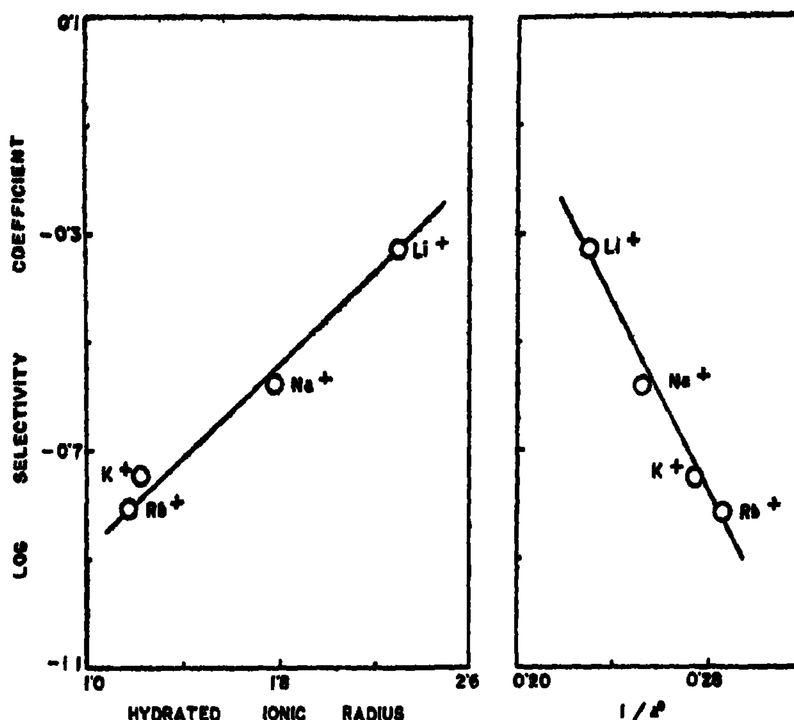


Fig. 2. Plots showing correlation of selectivity coefficient against hydrated ionic radius and the reciprocal of the Debye Hückel parameter, a°, in aqueous medium

been calculated from the equation $\lambda_i = \frac{\bar{m}_i}{m_i}$, where $\bar{m}_i$ and m_i are the concentrations of the species i in the solid and aqueous phases. According to these values (Table 1) the exchanging ability of the ions in pure aqueous medium may be placed in the sequence: $NH_4 > Li > Na > K > Rb > Cs$. The greater desorbing power of NH_4^+ is possibly due to the low pH of NH_4Cl solution in the concentration range studied where the high exchangeability of H^+ comes into play.

TABLE 1—EXCHANGE PROPERTIES OF $Co(tn)_3^{3+}$ FROM $Na\text{-}Co(tn)_3$-IRC-50 AGAINST VARIOUS MONOVALENT IONS IN AQUEOUS MEDIUM

Electrolyte used	Concentration of the electrolyte (M)	Distribution coefficient	Selectivity coefficient
LiCl	0.25	4.12	0.472
	0.40	3.86	0.590
	0.50	3.88	0.588
NaCl	0.25	2.66	0.259
	0.40	3.02	0.369
	0.50	3.27	0.458
KCl	0.25	2.05	0.179
	0.40	2.18	0.236
	0.50	2.47	0.305
RbCl	0.25	1.80	0.158
	0.40	1.96	0.202
	0.50	2.11	0.245
CsCl	0.25	1.68	0.184
	0.40	1.60	0.179
	0.50	2.05	0.285
NH_4Cl	0.25	5.85	0.772
	0.30	5.69	0.847
	0.40	6.10	1.010

In an attempt to correlate the relative affinities of the desorbing ions for the resin matrix with their sizes, plots of log(selectivity coefficient) against hydrated ionic radius[18] and the reciprocal of the Debye Hückel parameter[19], a°, i.e. the distance of closest approach between the counter ion and the fixed ionic group, have been made (Fig. 2). The latter plot is, however, on the basis of the simple electrostatic model of Pauley[20] which assumes that coulombic interaction between the counter ions and the fixed ionic groups is the predominant factor and the counter ions in the ion exchanger are found at their distance of closest approach to the fixed ionic groups. It is interesting to note that both the parameters give linear relation suggesting that both hydrated ionic radius as well as $\frac{1}{a}$ may be used for correlating the relative selectivities of the monovalent ions for the resin.

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Studies on Metal Chelates of 5-Iodo-8-Hydroxyquinolino-4-(*p*-Tolyl)sulphonamide and 5-Iodo-7-Chloro-8-Hydroxyquinolino-4-(*p*-Tolyl)sulphonamide as Potential Drugs

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Metal chelates of 5-iodo-8-hydroxyquinolino-4-(p-tolyl)sulphonamide [IHQTS] and 5-iodo-7-chloro-8-hydroxyquinolino-4-(p-tolyl)sulphonamide [ICHQTS] with metals like Fe(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) have been synthesized and characterized by elemental analyses and ir spectra. They were screened for their antibacterial activity against gram positive bacteria *S aureus* and gram negative *E. coli* to test the change in antibacterial activity of ligands on complexation.

THE chemistry of quinoline and *p*-toluene sulphonamide have attracted special attention because of their therapeutic properties[1-3]. Some of the sulphonamides were used as drugs for diseases like cancer[3], tuberculosis[4], diabetes[5], malaria[6], leprosy[7] and convulsion[8]. They were found to be active against different types of bacteria. It has been observed recently that some drugs have increased activity when administered as metal complexes, more so their metal chelates[9-10]. A similar indication was also found in our previous study[11]. In continuation of our previous work and to test the change in antibacterial activity of ligands on chelation, we report here the synthesis of metal chelates of IHQTS and ICHQTS with Fe(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II).

Experimental

All the chemicals used were of AnalaR grade and recrystallized. The metal-ligand ratio was determined by conductometric titrations and Job's method of continuous variation, which showed 1 : 2 complexation. Infrared spectra were recorded on an automatic Perkin-Elmer 577 spectrophotometer in KBr phase. Metals were estimated by standard methods[12], sulphur by modified Messenger's method[13] and nitrogen by modified Kjeldahl's procedure[14].

Ligands : The ligands IHQTS and ICHQTS were prepared by the action of chlorosulphonic acid on 5-iodo-8-hydroxyquinoline and 5-iodo-7-chloro-8-hydroxyquinoline, thus getting their sulphonyl chlorides. These sulphonyl chlorides were then allowed to react with *p*-toluidine in ethanolic medium. This resulted in the formation of precipitates of IHQTS and ICHQTS respectively. The precipitates were filtered, washed well with ethanol and recrystallized.

Complexes : IHQTS and ICHQTS were dissolved in warm distilled water and treated with an appropriate amount of metal salt solution in distilled water at a *p*H ranging from 8-9. The *p*H was maintained by using a solution of 8.50 ml to 21.30 ml of 0.1 *N* NaOH and 50 ml of 0.1 *M* H_3BO_3. The resulting precipitates of the complexes were filtered, washed well with hot distilled water and dried in an oven at 110-120°.

Infrared spectra. A broad distinct band at 2950 cm^{-1} in the spectrum of IHQTS and another at 3100 cm^{-1} in ICHQTS were found. These values are less than the prescribed limit (3700-3300 cm^{-1}) for –OH group. It is due to hydrogen bonding[15-16]. On this basis the intramolecular hydrogen bonded chelate structures (–O–H N–) have been proposed for the ligands. A critical examination of the spectra of metal chelates indicates that the bands at 2950 cm^{-1} and 3100 cm^{-1} present in the ligands shift to higher values (3600-3300 cm^{-1}) in the chelates. Thus on metal chelate formation, the bands between 3600-3300 cm^{-1} which appear in all chelates are not present in the original ligands[17,18]. The disappearance of H—bonded –OH in the ligands and its reappearance in the metal chelates are suggestive of O–M–N bond formation, where M is a metal atom. The bands of medium intensity around 1600 cm^{-1} in the spectra of ligands due to ν(>C=N–) shift to lower values with weak intensity in the spectra of chelates. It is due to M←N bond formation. The bands between 1600-1490 cm^{-1} are due to aromatic rings. The sharp bands around 500 cm^{-1} and 800 cm^{-1} are due to $-\overset{|}{\underset{|}{C}}-I$ and $-\overset{|}{\underset{|}{C}}-Cl$ respectively[19]. The presence of sulphonamide group has been established by a characteristic band in the vicinity of the region 1370 cm^{-1} [20,21].

Results and Discussion

The results of analyses and colour of the chelates are recorded in Table 1.

TABLE 1

Compound	Colour	%N Found (Calcd.)	%S Found (Calcd)	%M Found (Calcd.)	%I Found (Calcd.)	%Cl Found (Calcd.)
Fe-IHQTS	Brown	6.00 (5.99)	6.89 (6.85)	5.97 (5.98)	27.16 (27.19)	
Co-IHQTS	Light blue	5.98 (5.97)	6.85 (6.83)	6.90 (6.29)	27.08 (27.10)	
Ni-IHQTS	Green	5.91 (5.97)	6 80 (6.83)	6.30 (6 26)	27.10 (27.11)	
Cu-IHQTS	Light blue	5.90 (5.94)	6.81 (6.79)	6.71 (6.74)	26.91 (26.97)	
Cd-IHQTS	White	5.64 (5.65)	6 47 (6.46)	11.38 (11.34)	25 62 (25.64)	
Pb-IHQTS	Yellow	5.16 (5.16)	5.92 (5.89)	19.11 (19.09)	23.41 (23 40)	
Fe-ICHQTS	Light brown	5.56 (5.58)	6.42 (6 38)	5.56 (5.57)	25.31 (25 82)	7 01 (7.07)
Co-ICHQTS	Blue	5.57 (5.56)	6.43 (6.36)	5 85 (5.86)	25.27 (25.24)	7.10 (7.05)
Ni-ICHQTS	Light green	5.55 (5.56)	6.37 (6.36)	5.85 (5.83)	25.26 (25.25)	7.06 (7 05)
Cu-ICHQTS	Blue	5.58 (5.54)	6.32 (6.33)	6 29 (6 28)	25.10 (25.18)	7.00 (7 02)
Cd-ICHQTS	White	5 30 (5.28)	6.07 (6.04)	10.65 (10.60)	28.94 (28 97)	6 64 (6.70)
Pb-ICHQTS	Light yellow	4.87 (4.85)	5.57 (5.54)	17.99 (17.95)	21 96 (22.00)	6.10 (6 15)

The overall study and the analytical data given in Table 1 show that both the ligands form chelates of the type ML_2 where L = ligand. Hence a composition of the type $M(C_{16}H_{12}SN_2O_3I)_2$ and $M(C_{16}H_{11}SN_2O_3ICl)_2$ may be given for the metal chelates of IHQTS and ICHQTS respectively.

The reaction for IHQTS may be written as in Fig. 1. A similar reaction can be written for

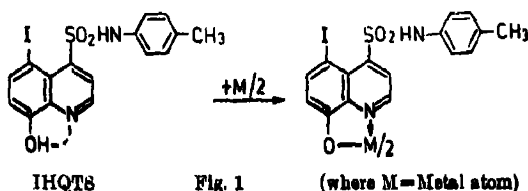


Fig. 1

ICHQTS also. The structure of the metal chelate is in good agreement with past workers[22,23].

The exact melting points could not be determined but were more than 300°.

Screening for antibacterial activity : The bacteriostatic properties of ligands and their metal chelates were studied by the usual cup-plate agar diffusion technique[24] against *S. aureus* and *E. coli.* 1.0% (w/v) solutions[25,26] of the compounds were prepared. A mixture of equal volumes of isopropyl alcohol and dioxan was taken and its 20% solution was used as solvent. Four holes (about 5 mm diam) were cut in the agar medium enriched with culture and 0.1 ml of 1.0% solution of the compounds were put in these holes. The petridishes were allowed to remain in the refrigerator at 4-8° for about 1 hr to allow the diffusion of the solutions. These petridishes were then transferred to an incubator maintained at 37° and the zones of inhibition were noted after 24 hr of incubation by measuring with callipers. The control with solvent under identical conditions showed no activity. The results are given in Table 2

TABLE 2

Sl. No.	Compound	Zone of inhibition in mm *S. aureus*	*E. coli*	Sl. No	Compound	Zone of inhibition in mm *S. aureus*	*E. coli*
1.	IHQTS	10	—	8	ICHQTS	15	15
2.	Fe-IHQTS	24	24	9	Fe-ICHQTS	26	27
3.	Co-IHQTS	—	21	10.	Co-ICHQTS	29	—
4.	Ni-IHQTS	23	28	11.	Ni-ICHQTS	21	21
5.	Cu-IHQTS	25	24	12	Cu-ICHQTS	26	25
6.	Cd-IHQTS	20	—	13.	Cd-ICHQTS	—	—
7.	Pb-IHQTS	24	—	14.	Pb-ICHQTS	24	24

Compound No. 1 showed a little activity towards *S. aureus* and no activity towards *E. coli*, while compound No. 8 showed activity against both the organisms. Compound No. 3 showed no activity against *S. aureus* while compounds No. 6, 7 and 10 showed no activity against *E. coli* but were active against *S. aureus*. Compound No. 13 showed no activity against both the organisms. We can thus, in general say that antibacterial activity is enhanced on complexation of IHQTS and ICHQTS with metals.

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Synthesis of Some Aryl Fluorobenzene Sulphonates and Hydroxy Diaryl Sulphones as Potential Fungicides

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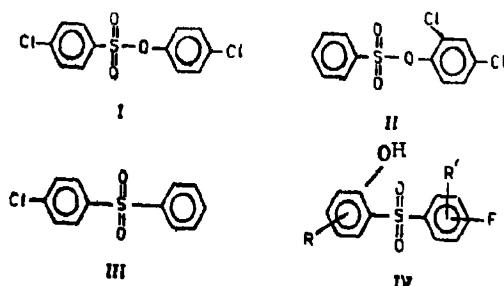
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Several aryl fluorobenzene sulphonates have been prepared by the interaction of fluorobenzene sulphonylchloride and appropriate phenols. Some of these esters were subjected to Fries transformation in presence of anhydrous $AlCl_3$ in absence of solvent to give hydroxy diaryl sulphones. All these compounds have been tested against two species of fungi, viz. *Helminthosporium oryzae* and *Aspergillus niger* and their fungitoxicity have been compared with that of Dithane M-45, a commercial fungicide. While some of the sulphones exhibit fungitoxicity comparable to the commercial fungicide at concentrations of 1000 ppm and 100 ppm, all compounds under investigation turn out to be very weak fungicides at a concentration of 10 ppm.

THE esters of aromatic sulphonic acids often display high physiological activity[1]. The commercialisation of Ovotran (I)[1,2,3] and Genite (II)[4] as pesticides is an ample proof of biological versatility of such esters. Similarly, diaryl sulphones such as sulphenone[5] (III) also exhibit pesticidal properties. However, similar data on fluoro and mixed halobenzene sulphonic acid ester and related hydroxy sulphones appears to be lacking except some preparative work reported by us earlier[6].

In view of these and also the observation that introduction of fluorine often imparts fungitoxicity in aromatic systems[7,8,9], it was anticipated that the aryl esters of fluoro and mixed halo benzene sulphonic acid (IV) might be an useful pesticide and also the hydroxy sulphones (IV) by virtue of possessing the kerolytic phenolic –OH group and the essential features of sulphenone (III) might have enhanced pesticidal properties.



The arylfluorobenzene sulphonates were prepared by reacting fluorobenzene sulphonyl-chlorides with appropriate phenol in acetone alkali solution in cold[6]. The fluorobenzene sulphonyl chlorides were prepared by chlorosulphonation of fluorobenzenes following the methods of Huntress and Carten[10]. The fluoroaromatic hydrocarbons were prepared essentially by Balz-Schiemann reaction[11]. The hydroxy diarylsulphones were obtained by the Fries transformation of arylfluorobenzene sulphonates at 130-40° in presence of anhydrous $AlCl_3$.

The significant bands in ir spectra of sulphonates were, 1160-1200 cm^{-1} ($O-SO_2-$ sym. stretching) and 1010-1040 cm^{-1} (C–F stretching) in addition to bands around 1600, 1550 and 1475 cm^{-1}, characteristic of aromatic ring. For the hydroxy sulphones, it revealed bands around 1300-1333 cm^{-1} ($-SO_2-$ asym. stretching), 1100-1145 cm^{-1} ($-SO_2-$ sym. stretching) and an intense peak at 3300-3340 cm^{-1} due to phenolic –OH stretching. Presence of this –OH peak indicates the conversion of sulphonates into hydroxy sulphones.

Experimental

Fluorohydrocarbons : 4-Fluorotoluene[12] b.p. 118-20°, 3-fluorotoluene[13] b.p. 116° and 4-chlorofluorobenzene[13] b.p. 130°/756 mm were prepared from *p*-toluidine, *m*-toluidine and *p*-chloroaniline respectively by Balz-Schiemann reaction.

Arylsulphonyl chlorides : 2-Methyl-5-fluorobenzene sulphonyl chloride[10] b.p. 170-72°/40 mm, 2-methyl-4-fluorobenzenesulphonyl chloride[10] b.p. 150-52°/92 mm and 2-chloro-5-fluorobenzene sulphonylchloride[10] b.p. 205°/10 mm were prepared by chlorosulphonation of appropriate fluorohydrocarbons following the method of Huntress and Carten.

These were characterised as sulphonamides.

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Arylfluorobenzene sulphonates : To an ice-cold solution of arylsulphonyl chloride (1.1 *M*) and phenol (1 *M*) in acetone, was added a slight excess of NaOH solution (10%) with frequent shaking. The sulphonates thus separating were washed free of alkali and recrystallised from aqueous ethanol. The compounds thus prepared are recorded in Table 1.

TABLE 1

Sl. No.	R	R_1	R_2	R_3	R_4	m.p °C
1.	5-F	CH_3	Cl	Cl	H	65
2.	5-F	CH_3	Cl	H	H	53
3	5-F	CH_3	CH_3	CH_3	H	91
4.	5-F	CH_3	H	Cl	H	68
5.	5-F	CH_3	H	H	H	62
6.	4-F	CH_3	CH_3	CH_3	H	51
7.	4-F	CH_3	Cl	H	H	82
8.	4-F	CH_3	H	H	Cl	80
9.	5-F	Cl	Cl	Cl	H	54
10.	5-F	Cl	H	Cl	H	66
11.	5-F	CH_3	Cl	Cl	H	165
12.	5-F	CH_3	Cl	H	H	114
13	5-F	CH_3	H	Cl	H	210
14.	4-F	CH_3	CH_3	CH_3	H	170
15.	5-F	Cl	Cl	Cl	H	190

Satisfactory elemental analysis were obtained for all the compounds.

Hydroxy diarylsulphones : A mixture of arylfluorobenzene-sulphonate (0.1 *M*) and anhydrous $AlCl_3$ (0.15 *M*) was heated till a melt was formed. Heating of the melt was continued for 3-4 hr at 130-40°. The reaction mixture was decomposed with crushed ice and HCl. The product separating was taken into ether and purified as usual. The sulphones thus prepared are recorded in Table 1.

Fungicidal activity : The fungicidal activity was evaluated by agargrowth technique[14] on *H. oryzae* and *A. niger* at three different concentrations, 1000 ppm, 100 ppm and 10 ppm. With a view to compare the results, a commercial fungicide Dithane M-45 was also tested under similar conditions.

The fungicidal data of compounds under investigation reveal that the sulphonate esters as a class are very weak fungicides. The hydroxy sulphones are toxic to both *H. oryzae* and *A. niger* at higher concentrations (1000 ppm and 100 ppm). The activity is particularly more pronounced in those sulphones which contain chloro substituents in *para* and *ortho*-positions or both. However, all these compounds prove to be weaker fungicides at a concentration of 10 ppm.

The presence of fluorine does not in any way enhance the toxicity of such compounds. The mixed halo derivatives, however, have better performance as fungicide than those containing fluoro or chloro separately. It is noteworthy that the fungitoxicity of the compounds is greater towards *A. niger* than *H. oryzae*.

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Synthesis of 4-Imidazolyl-2-Methyl-5-Nitro-8-Hydroxy Quinolines as Possible Antiprotozoal Agents

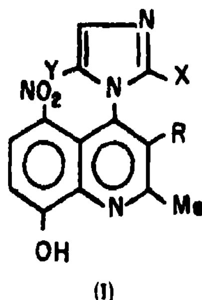
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4-Chloro-2-methyl-5-nitro-8-hydroxy quinolines were condensed with imidazole and its derivatives to obtain 4-imidazolyl-2-methyl-5-nitro-8-hydroxy quinolines having no significant antiprotozoal activity.

OBSERVATION of antiprotozoal activity[1,2] of metronidazole [1-(2-hydroxy-ethyl)-2-methyl-5-nitroimidazole] and 5-nitro-8-hydroxy quinolines prompted us to synthesise compounds of the type (I) to examine their amebicidal and trichomonacidal activity. Such compounds possess both the features of 8-hydroxy quinoline and imidazole.



(I)

These compounds have been prepared by treating an appropriate 4-chloro quinoline with an imidazole derivative in presence of phenol. 2-Methyl-4-chloro-5-nitro-8-hydroxy quinolines have been prepared by demethylation of the corresponding 8-methoxy quinoline with 2 *N* NaOH. 4-Chloro-2-methyl-5-nitro quinolines and the corresponding 7-nitro isomers have been prepared by nitration of 2-methyl-4-chloro-8-methoxy quinoline with concentrated HNO_3 in H_2SO_4 medium which gave a dinitro derivative along with two mononitro compounds. The 5-nitro compound (m.p. 113-14°) has been separated out from the mixture of mononitro quinolines by fractional crystallisation. The structure of this nitro compound has been proved by the fact that dehalogenation and conversion of the nitro group to chloro gave chloro-2-methyl-8-methoxy quinoline which was found to be identical with that of an authentic sample of 5-chloro-2-methyl-8-methoxy quinoline. Similarly, 2-methyl-3-*n*-propyl-4-chloro-8-methoxy quinoline was nitrated to a mixture of dinitro and corresponding 5-nitro and 7-nitro quinolines. The dichloro compound, obtained on conversion of the 5-nitro compound, was found to be identical with an authentic sample of 2-methyl-3-*n*-propyl-4,5-dichloro-8-methoxy quinoline prepared in this laboratory[3].

Biological activity : None of the compounds described in this paper was found to be significantly active *in vitro* against *E. histolytica*, *T. vaginalis* and *T. foetus* at a concentration of 12.5 mg/ml. An explanation of the absence of significant activity may be that the geometry of these molecules perhaps does not favourably fit with the geometry of the active site of the enzyme system of the microorganism involved in the interaction.

Experimental

2-Methyl-4-chloro-5-nitro-8-methoxy quinoline and 2-methyl-4-chloro-7-nitro-8-methoxy quinoline : Conc. HNO_3 (13 ml) was slowly added to an ice cooled and stirred solution of 2-methyl-4-chloro-8-methoxy quinoline (13 g) dissolved in conc. H_2SO_4 (32.5 ml) over half an hour. The solution was then poured on crushed ice under stirring. A yellow solid (1.5 g) separated out. It was collected by filtration, washed with dilute NH_4OH and crystallised from a large volume of ethyl alcohol to yield a dinitro derivative, m.p.>300° (decomp.). Found. N, 13.81. Calculated for $C_{11}H_8N_3O_5Cl$; N, 14.11%.

The filtrate was neutralised with NH_4OH and the separated yellow solid was collected by filtration. This solid (15 g) was a mixture of 5-nitro and 7-nitro derivatives which were separated by fractional crystallisation from aqueous ethyl alcohol (1 : 1) when the more soluble fraction was isolated, m p 113-14° ; yield 9.4 g (60%). Found : C, 51.85, H, 3.17 ; N, 10.64. Calculated for $C_{11}H_9N_2O_3Cl$; C, 52.31 ; H, 3.56 ; N, 11.08%. The structure of the compound was proved to be 2-methyl-4-chloro-5-nitro-8-methoxy quinoline.

The residual mass was crystallised from absolute alcohol, m.p. 150-51° ; yield 1.56 g (10%). Found : C, 51.90 ; H, 3.?7 ; N, 10.68. Calculated for $C_{11}H_9N_2O_3Cl$; C, 52.31 ; H, 3.56 ; N, 10.08%.

5-Amino-2-methyl-8-methoxy quinoline : 2-Methyl-4-chloro-5-nitro-8-methoxy quinoline (4 g) was dissolved in absolute alcohol (100 ml) and was hydrogenated at room temperature in presence of Pd/C (0.1 g). The catalyst was filtered off and the solvent removed from the filtrate. The residue was treated with dil. NH_4OH. The base was extracted

with ether, dry ethereal HCl was added to it when a solid was obtained. It was crystallised from a mixture of ethyl alcohol and ethyl acetate, m.p. 211-12°. Found : N, 10.81. Calculated for $C_{11}H_{14}N_2OCl_2$; N, 10.72%.

The above hydrochloride was dissolved in water and neutralised by liquor NH_3 when a light yellow solid was obtained. It was crystallised from a mixture of benzene and petroleum ether (60-80°) to a colourless compound, m p. 148-49° ; yield 90% (2.5 g). Found : C, 70.01 ; H, 6.18 ; N, 14.35. Calculated for $C_{11}H_{12}N_2O$; C, 70.20 ; H, 6.38 ; N, 14.8%.

2-Methyl-5-chloro-8-methoxy quinoline : 2-Methyl-5-amino-8-methoxy quinoline dihydrochloride (0.5 g) was dissolved in a mixture of conc. HCl (1 ml) and water (4 ml) and cooled to 0°. A solution of $NaNO_2$ (0.3 g) in water (1 ml) was added slowly to the above solution. A mixture of $CuSO_4.5H_2O$ (1 g), NaCl (0.5 g), copper turnings (0.5 g), conc.HCl (4 ml) and water (12.5 ml) was boiled until the solution was colourless. To this well cooled Cu_2Cl_2 solution was added slowly under stirring the cold diazotised solution, when the reaction proceeded with frothing. Stirring was continued for another 2 hr and the solution was left overnight. The solution was then filtered, washed, made alkaline with liquor NH_3 in cold when a solid separated out. The solid was filtered, washed and dried and purified further by crystallisation from petroleum ether (40-60°), m.p. 93° ; yield 0.11 g (20%). Found : C, 63.21 ; H, 4.35 , N, 6 5. Calculated for $C_{11}H_{10}NOCl$; C, 63.61 , H, 4.81 , N, 6.74%. It was found to be identical with an authentic sample of 2-methyl-5-chloro-8-methoxy quinoline (m.p. 93°)[8].

2-Methyl-4-chloro-5-nitro-8-hydroxy quinoline : 2-Methyl-4-chloro-5-nitro-8-methoxy quinoline (3 g) was refluxed with 2 *N* NaOH (300 ml) for 4 hr[4]. The solution was then acidified with AcOH when a yellow solid separated out. It was collected by filtration, dried and then heated with $POCl_3$ (50 ml) in an oil bath for half an hour at 120-130°. Subsequent pouring in ice-water and basification with liquor NH_3 yielded a yellow solid which crystallised as needles from petroleum ether, m.p. 160-61° ; yield 2 g (70%) ir (KBr) 3350 cm^{-1} (OH). Found : C, 50.2 ; H, 2.45 ; N, 11.52. Calculated for $C_{10}H_7O_3N_2Cl$; C, 50.3 ; H, 2 93 , N, 11.73%.

2-Methyl-3-n-propyl-4-chloro-5-nitro quinoline and 2-methyl-3-n-propyl-4-chloro-7-nitro quinoline : 2-Methyl-3-*n*-propyl-4-chloro-8-methoxy quinoline (5 g) was dissolved in conc. sulphuric acid (12 5 ml). The solution was cooled in ice and conc. HNO_3 (5 ml) was added to it with stirring over half an hour. Stirring was continued for another hour and the resultant mixture added to crushed ice. A yellow solid (0.3 g) separated out which was filtered, washed with dilute NH_4OH and crystallised from large volume of ethyl alcohol, to yield a dinitro derivative m.p. > 300° (decomp.). Found : N, 12.12. Calculated for $C_{14}H_{14}O_5N_3Cl$; N, 12.37%.

The filtrate was then neutralised with dilute NH_4OH and was made alkaline to phenolphthalein. A yellow solid separated out and was collected by filtration. The solid (5.5 g) was a mixture of 5-nitro and 7-nitro derivatives. They were separated by fractional crystallisation from aqueous ethyl alcohol (1 : 1), whereby the more soluble fraction, m.p. 136-37° was isolated; yield 1.8 g (30%). Found : C, 56.58 ; H, 5.1 ; N, 9.58. Calculated for $C_{14}H_{15}O_3N_2Cl$; C, 57.04 ; H, 5.09 ; N, 9.5%. The structure of the compound was proved to be 2-methyl-3-*n*-propyl-4-chloro-5-nitro-8-methoxy quinoline.

The residual mass was crystallised from absolute alcohol, m.p. 214-15° ; yield 3.5 g (59%). Found : C, 57.00 ; H, 4.59 ; N, 9.05. Calculated for $C_{14}H_{15}O_3N_2Cl$; C, 57.04 ; H, 5.09 ; N, 9.5%. The compound was probably 2-methyl-3-*n*-propyl-4-chloro-7-nitro-8-methoxy quinoline.

2-Methyl-3-n-propyl-4-chloro-5-amino-8-methoxy quinoline : A mixture of 2-methyl-4-chloro-5-nitro-8-methoxy quinoline (1.4 g), conc. HCl (15 ml) and $SnCl_2.2H_2O$ (5.64 g) was refluxed in an oil bath for 4 hr. A clear solution formed at first but finally solids separated out. The contents were dissolved in water (100 ml) and H_2S gas was passed through the solution until complete precipitation of tin was effected. The tin sulphides were removed by filtration and the filtrate was boiled to remove H_2S. The solution was cooled and made alkaline with liquor NH_3. The separated solid was filtered, dried and crystallised from a mixture of benzene-petroleum ether (60-80°) (1 : 1) in yellow needles, m.p. 92-93° ; yield 1.18 g (90%). Found : C, 63.25 ; H, 5.95 ; N, 10 1. Calculated for $C_{14}H_{17}N_2OCl$; C, 63.5 ; H, 6.4 ; N, 10.5%.

2-Methyl-3-n-propyl-4,5-dichloro-8-methoxy quinoline : 2-Methyl-3-*n*-propyl-5-amino-4-chloro-8-methoxy quinoline (1.3 g) was diazotised and treated with Cu_2Cl_2 in the usual manner. The product was purified by chromatographic method over silica gel using petroleum ether (40-60°) as an eluent, yield 0 35 g (25%). Found : C, 58.71 ; H, 5.1 ; N, 4.63. Calculated for $C_{14}H_{15}NCl_2O$: C, 59.1 ; H, 5.2 ; N, 4.9%

2-Methyl-3-n-propyl-4-hydroxy-5-chloro-8-methoxy quinoline : A mixture of 5-chloro-*o*-anisidine (15 g) and ethyl *n*-propyl acetoacetate (18 g) was treated with[4] a few drops of dilute (1 : 1) HCl and the mixture kept overnight. Dry benzene (100 ml) was then added to it and the mixture heated in an oil bath at 130-140° in a Dean-Stark apparatus till no more water collected. Benzene was removed by distillation. The residual viscous mass was poured dropwise into boiling diphenyl oxide (500 ml) and boiled for 15 min. The reaction mixture was cooled and diluted with petroleum ether (60-80°). The separated solid was filtered and crystallised from dilute ethyl alcohol, m.p. 215-16° ; yield 10 g (39%).

2-Methyl-3-n-propyl-4,5-dichloro-8-methoxy quinoline : The above 4-hydroxy quinoline (10 g) was

heated under reflux with a mixture of $POCl_3$ (21 ml) and PCl_5 (1.8 g) in an oil bath[3] at 130-33° for 5-6 hr. The product was cooled, decomposed with ice, made alkaline with NH_4OH. The precipitated solid was filtered, thoroughly washed with water and crystallised from a mixture of benzene and petroleum ether (60-80°) (1 : 1), m.p. 107-108°; yield 7 g (65%). Found : C, 58.75 ; H, 5.1 ; N, 4.52. Calculated for $C_{14}H_{15}ONCl_2$; C, 59.1 ; H, 5.2 ; N, 4.9%.

2-Methyl-3-n-propyl-4-chloro-5-nitro-8-hydroxy quinoline : 2-Methyl-3-*n*-propyl-4-chloro-5-nitro-8-methoxy quinoline (1.25 g) was refluxed with 2 *N* NaOH (125 ml) for 24 hr[4]. The solution was acidified with AcOH when a yellow solid separated which was filtered, dried and refluxed with $POCl_3$ (25 ml) in an oil bath for half an hour at 120-130°. Finally, the mass was poured in ice-water and made alkaline with liquor NH_3. The product was treated with charcoal when a yellow solid (0.5 g) separated; yield 0.5 g (48%). It crystallised in needles from petroleum ether (60-80°), m.p. 124-25°, ir (KBr) 3375 cm^{-1} (OH). Found : C, 55.25 ; H, 4.25 ; N, 9.5. Calculated for $C_{13}H_{13}O_3N_2Cl$; C, 55.65 ; H, 4.63 ; N, 9.88%.

General method for preparing 4-imidazolyl-2-methyl-5-nitro-8-hydroxy quinolines : A mixture of 4-chloroquinoline derivatives (0.005 mole), imidazole or its derivatives[6] (0.005 mole) and phenol (4 ml) was refluxed in an oil bath for 24 hr at about 200°. It was then acidified with dil. HCl and extracted with ether to remove phenol. Aqueous HCl was separated out and it was made alkaline with liquor NH_3 when a solid separated. The solid was collected by filtration, washed with water, dried and crystallised from a suitable solvent. Using this method the following compounds were prepared :

I(X=Y=R=H), m.p. 102-103°[a]. Yield 40%
I(X=R=H ; Y=NO_2) m.p. 85-86°[b]. Yield 40%
I(X=Me ; Y=R=H), m.p. 98-99°[b]. Yield 45%
I(X=Me ; Y=NO_2 ; R=H), m.p. 129-30°[b]. Yield 40%
I(X=Y=H ; R=*n*-C_3H_7), m.p. 101-102°[b]. Yield 36%

(a) Crystallised from aqueous ethanol ; (b) crystallised from a mixture of benzene and petroleum ether (60-80°) (1 : 1) in yellow needles and gave satisfactory C, H, N analyses.

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Synthesis of Some New 4(3H)Quinazolinones as Potential Fungicides

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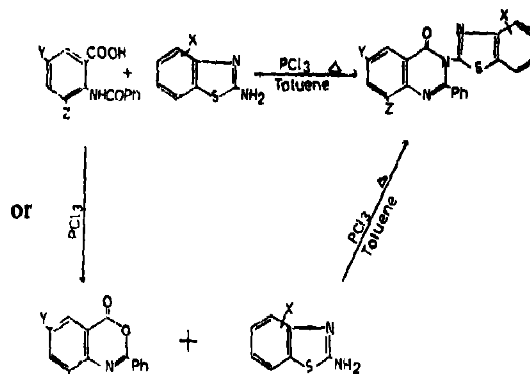
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Several 6,8-disubstituted-2-phenyl-3[(substituted)benzothiazol-2'-yl]-4(3H)quinazolinones have been synthesised. Their fungicidal activity has been screened on *Aspergillus fumigatus* and *Alternaria alternata*. 6-Methyl, 5 and 6-chloro substituted derivatives have been found to be very good fungicides.

SEVERAL biological activities have been reported in 4(3H)quinazolinones[1-5] which have been successfully screened as antihypertensives[6], chlorectic, antifibrillatory, antiphlogistic, hypotensive[7], antiadronergic, antihistaminic[8], antifungal[9-10], herbicidal[11] and bactericidal[12] agents. Febrifugine, an alkaloid with a 3-substituted 4(3H) quinazolinone structure has been found to be antimalarial[13]. Siamian and avian malarial infections have also been successfully treated with them[14,15]. Viricidal activity has been reported in some nitro substituted 4-quinazolinone derivatives[16]. Oine *et al*[17] have prepared some quinazolinones with antiulcer, CNS depressant and analgesic action. Some piperizino quinazolinones as cardiovascular, hypotensive, noradrenalin inhibiting, brady-cardiac and trachycardiac agents have recently been reported by Dubey *et al*[18]. Antitumour and anticancerous actions have also been observed in 2-alkyl-3-aryl-4-(3H)quinazolinone derivatives[19]. Hutchinson *et al*[20] have reported antileukemic activity in 4(3H) quinazolinone derivatives. The findings of Peck *et al*[21,22] and Creech *et al*[23] have considerably accelerated the investigation with this system.

Various heterocyclic systems have been attached to the quinazolinone system at positions two and three. The search for potential psychotropic agents led to the preparation of 2-(N[4]-arylpiperazino carbonylmethylthio)-3-aryl-6-bromo-4(3H) quinazolinones[24]. Recently Pandey *et al*[25] have synthesised 2-aryl (or alkyl)-3-(2'-aminomethyl-1', 3', 4'-thiadiazol-5'-yl)quinazol-4(3H)-ones as potential antiparkinsonian compounds. Amoebicidal and fungicidal activities have been reported in some quinazolinone derivatives by Gupta *et al*[26].

Keeping in view the wide spectrum activities of this system it was considered worthwhile to synthesise some 4(3H)quinazolinones incorporating the substituted benzothiazole moiety at position three as possible antifungal agents. The compounds were prepared according to the scheme outlined below :



6, 8-Disubstituted-2-phenyl-3-[(substituted)benzothiazol-2'-yl)]-4(3H)quinazolinones were obtained through benzoxazinone intermediate by refluxing substituted 2-amino benzothiazoles with 3, 5-disubstituted N-benzoyl anthranilic acids and phosphorous trichloride in toluene for 4 hr. The structure was confirmed by elemental analysis, ir and nmr spectra.

Experimental

All melting points were recorded in open capillary in liquid bath and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, nmr on Varian A-60 D Model at 60 Hz at 45°. A Coleman analyser was used for elemental analysis.

N-Benzoylanthranilic acid and 3,5-dibromo-N-benzoylanthranilic acid were prepared by known methods[28,29].

Substituted 2-amino benzothiazoles : These were prepared by the oxidation of asymmetrical aryl thiourea with liquid bromine in chloroform[30].

6,8-Dibromo-2-phenyl-3-(6'-ethoxy benzothiazol-2'-yl)-4(3H)quinazolinone : A mixture of benzoyl anthranilic acid (7.5 g), 2-amino-6-ethoxy benzothiazole (3.30 g), phosphorous trichloride (1.5 ml)

TABLE 1—6,8-DISUBSTITUTED-2-PHENYL-3[(SUBSTITUTED)BENZOTHIAZOL-2'-YL]-4(3H)QUINAZOLINONES

Sl. No.	Substituents X	Y=Z	Molecular Formula	Yield %	m.p °C	Carbon % Found	Carbon % Calcd.	Hydrogen % Found	Hydrogen % Calcd.
1.	H	H	$C_{21}H_{13}N_3OS$	65	101	71.16	70.98	3.70	3.66
2.	5-Me	H	$C_{22}H_{15}N_3OS$	81	187	71.75	71.54	3.89	4.06
3.	6-Me	H	$C_{22}H_{15}N_3OS$	89	167	70.27	71.54	4.26	4.06
4.	5-Cl	H	$C_{21}H_{12}ClN_3OS$	46	120	64.41	64.69	3.89	3.08
5.	6-Cl	H	$C_{21}H_{12}ClN_3OS$	49	115	64.56	64.69	2.99	3.08
6.	6-MeO	H	$C_{22}H_{15}N_3O_2S$	71	116	68 71	68.57	4.01	3.89
7.	6-EtO	H	$C_{23}H_{17}N_3O_2S$	76	150	68.92	69.17	4.40	4.26
8.	H	Br	$C_{21}H_{11}Br_2N_3OS$	61	184	48.88	49.12	2 01	2 14
9.	5-Me	Br	$C_{22}H_{13}Br_2N_3OS$	29	194	49.87	50 09	2.39	2.46
10.	6-Me	Br	$C_{22}H_{13}Br_2N_3OS$	83	198	49.99	50.09	2.61	2.46
11.	5-Cl	Br	$C_{21}H_{10}Br_2ClN_3OS$	49	170	45.23	45.56	2.01	1.82
12.	6-Cl	Br	$C_{21}H_{10}Br_2ClN_3OS$	62	205	45.87	45 56	2 11	1.82
13.	6-MeO	Br	$C_{22}H_{13}Br_2N_3O_2S$	69	146	48 42	48.62	2.56	2.39
14.	6-EtO	Br	$C_{23}H_{15}Br_2N_3O_2S$	73	169	49 59	49.55	2.81	2.69

and dry toluene was refluxed on water bath for 4 hr. Excess toluene was distilled off. The granular product was washed with 5% sodium bicarbonate solution and distilled water. It was filtered, dried and recrystallised from ethanol to give 6,8-dibromo-2-phenyl-3-(6'-ethoxy benzothiazol-2'-yl)-4(3H)-quinazolinone in 73% yield; m.p. 169°. Anal. Found : C, 49.59 ; H, 2.81 ; Calcd. for $C_{23}H_{15}Br_2N_3O_2S$; C, 49.55 ; H, 2.69%. IR (nujol) : 1765s, 1655m, 1600s, 1555m cm^{-1}. NMR ($CDCl_3$) : δ : (J=Hz), 1.45(3H, t, J=7.0), 4.10(2H, q, J=7.0) and 7.1 to 8.3 for aromatic protons (10H, m).

Other 2-phenyl-3-[(substituted)benzothiazol-2'-yl]-4(3H)quinazolinones and 6,8-dibromo-2-phenyl-3-[(substituted)benzothiazol-2'-yl]-4(3H)quinazolinones were prepared similarly. Their melting points, yields and analytical data are reported in Table 1.

Biological tests : The compounds 2-phenyl-3-[(substituted)benzothiazol-2'-yl]-4(3H)quinazolinones and 6,8-dibromo-2-phenyl-3-[(substituted)-benzothiazol-2'-yl]-4(3H)quinazolinones were tested for fungicidal action on *Alternaria alternata* and *Aspergillus fumigatus* by the agar plate technique[a7] at two dilutions.

The percent inhibition of growth was determined by comparison with growth in controls and the results are recorded in Table 2. All solutions were prepared in absolute alcohol. The medium in controls and the treated plates was potato dextrose agar culture medium and the incubation time 96 hr at 28±1°.

The results indicate that the activity of the compounds is of high order against both the species. The replacement of hydrogen by methyl, chloro, methoxy or ethoxy group increases the activity at both dilutions in case of the 2-phenyl derivatives. Fungicidal action decreases when the substituent is 6-methoxy in case of *Aspergillus fumigatus*. The decrease is slight at low and considerable at high dilutions.

The introduction of 6,8-dibromo group in the 4(3H)quinazolinone ring appears to enhance the antifungal properties considerably as compared to the non substituted derivatives. The compounds of 6,8-dibromo-2-phenyl-3-[(substituted)benzothiazol-2'-yl)]-4(3H)quinazolinones inhibit 100% spore germination of both the fungal species, especially at low dilutions and appear to be potent antifungal agents. Further testing of these compounds for CNS depressant activity is in progress.

TABLE 2—FUNGICIDAL SCREENING RESULTS OF 6,8-DISUBSTITUTED-2-PHENYL-3-[(SUBSTITUTED)-BENZOTHIAZOL-2'-YL]-4(3H) QUINAZOLINONES

Sl. No	Substituents X	Y=Z	*Alternaria alternata* Dilutions 1 : 1500		*Aspergillus fumigatus* Dilutions 1 : 1500	
			1 : 1500	1 : 3400	1 : 1500	1 : 3400
1	H	H	82	74	100	52
2.	6-Me	H	100	100	100	100
3.	5-Cl	H	100	78	100	61
4	6-Cl	H	100	100	100	100
5	6-MeO	H	100	74	82	39
6.	6-EtO	H	100	83	100	74
7.	H	Br	100	83	100	74
8.	5-Me	Br	100	67	100	91
9.	6-Me	Br	100	100	100	74
10.	5-Cl	Br	100	100	100	100
11	6-Cl	Br	100	79	100	100
12	6-MeO	Br	82	67	100	100
13.	6-EtO	Br	82	79	55	74

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Some New Coumarins and Schiff's Bases as Possible Antibacterial and Antifungal Agents

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Some new coumarins and Schiff's bases have been prepared by condensing different substituted malon-anilic acids with salicylaldehyde and substituted salicylaldehydes using different condensing agents. Some of the prepared compounds were screened for antibacterial and antifungal activity.

VARIOUS workers[1-4] have reported the pharmacological importance of coumarins and Schiff's bases. In view of this some new coumarins and Schiff's bases have been prepared by condensing malon-4-bromo-2-methyl, malon-4-bromo-3-methyl and malon-2-bromo-4-methyl anilic acids with salicylaldehyde, 5-chloro, 5-bromo, 5-nitro, 3,5-dichloro, 3,5-dibromo, 3,5-diiodo and 5-chloro-3-nitro salicylaldehyde. All these condensations were carried out in the presence of a trace of pyridine or piperidine or in the absence of any condensing agent. The purity and homogeneity of all the compounds were tested by tlc and elemental analysis.

Experimental

All the melting points are uncorrected. Malon-anilic acids used were prepared by the method of Singhal and Ittyerah[5].

Condensation of malon-4-bromo-2-methyl-anilic acid with salicylaldehyde : Formation of coumarin-3-carboxy-(4-bromo-2-methyl)anilide and 2-hydroxy benzal (4-bromo-2-methyl) aniline : Malon-4-bromo-2-methyl anilic acid (1.36 g ; 0.05 mol) and salicylaldehyde (0.6 g ; 0.05 mol) and a drop of pyridine were refluxed in oil bath for 4 hr at 110-20°. The yellow solid mass was then digested with saturated solution of sodium bicarbonate (10 ml). The alkali extract was decanted and the residue washed well with water. The alkali extract on acidification with HCl did not form any precipitate. The residue was boiled with ethanol (15 ml) and filtered. The ethanolic extract, on concentration and cooling, gave 2-hydroxy-benzal (4-bromo-2-methyl)aniline, m.p. 62°.

The identity of this product was further confirmed by synthesising an authentic specimen from 4-bromo-2-methyl aniline and salicylaldehyde.

The residue left after boiling with ethanol was recrystallised from glacial acetic acid as yellow crystals of coumarin-3-carboxy-(4-bromo-2-methyl)-anilide, m.p. 240°.

The other coumarins and Schiff's bases prepared by the above procedure alongwith their m.p. are recorded in Tables 1 and 2 respectively. The yield of the products varies from 4.82 to 44.69%

Antimicrobial activity of some of these compounds have been shown in the Tables.

TABLE 1

Sl. No.	Compound	Mol Formula	m.p. (°C)	Microbe (r/ml)
1.	6-chloro-R_1*	$C_{17}H_{11}O_3NBrCl$	246	—
2.	6,8-dichloro-R_1	$C_{17}H_{10}O_3NBrCl_2$	244	a(25)
3.	6-bromo-R_1	$C_{17}H_{11}O_3NBr_2$	242	—
4.	6,8-dibromo-R_1	$C_{17}H_{10}O_3NBr_3$	239	—
5.	6,8-diiodo-R_1	$C_{17}H_{10}O_3NBrI_2$	178	—
6	6-nitro-R_1	$C_{17}H_{11}O_5N_2Br$	190	—
7.	6-chloro-8-nitro-R_1	$C_{17}H_{10}O_5N_2BrCl$	227	—
8.	R_2*	$C_{17}H_{12}O_3NBr$	225	—
9.	6-chloro-R_2	$C_{17}H_{11}O_3NBrCl$	247	—
10.	6,8-dichloro-R_2	$C_{17}H_{10}O_3NBrCl_2$	252	—
11.	6-bromo-R_2	$C_{17}H_{11}O_3NBr_2$	250	—
12	6,8-dibromo-R_2	$C_{17}H_{10}O_3NBr_3$	186	—
13.	6,8-diiodo-R_2	$C_{17}H_{10}O_3NBrI_2$	171	—
14.	6-nitro-R_2	$C_{17}H_{11}O_5N_2Br$	198	—
15.	6-chloro-8-nitro-R_2	$C_{17}H_{10}O_5N_2BrCl$	208	—
16.	R_3*	$C_{17}H_{12}O_3NBr$	238	—
17.	6-chloro-R_3	$C_{17}H_{11}O_3NBrCl$	180	—
18.	6,8-dichloro-R_3	$C_{17}H_{10}O_3NBrCl_2$	246	a(50)
19.	6-bromo-R_3	$C_{17}H_{11}O_3NBr_2$	251	—
20	6,8-dibromo-R_3	$C_{17}H_{10}O_3NBr_3$	171	—
21.	6,8-diiodo-R_3	$C_{17}H_{10}O_3NBrI_2$	182	—
22.	6-nitro-R_3	$C_{17}H_{11}O_5N_2Br$	209	—
23.	6-chloro-8-nitro-R_3	$C_{17}H_{10}O_5N_2BrCl$	239	—

R_1* Coumarin-3-carboxy-(4-bromo-2-methyl)-anilide,
R_2* Coumarin-3-carboxy-(4-bromo-3-methyl)-anilide,
R_3* Coumarin-3-carboxy-(2-bromo-4-methyl)-anilide,
a = *M. tuberculosis*.

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TABLE 2

Sl. No.	Compound	Mol. Formula	m.p. (°C)	Microbe (γ/ml)
24.	5-chloro-R_1*	$C_{14}H_{11}ONClBr$	114	a(3.12)
25	3,5-dichloro-R_1	$C_{14}H_{10}ONCl_2Br$	106	a(3.12)
26.	5-bromo-R_1	$C_{14}H_{11}ONBr_2$	125	—
27.	3,5-dibromo-R_1	$C_{14}H_{10}ONBr_3$	180	—
28.	3,5-diiodo-R_1	$C_{14}H_{10}ONBrI_2$	198	—
29.	5-nitro-R_1	$C_{14}H_{11}O_3N_2Br$	195	—
30.	5-chloro-3-nitro-R_1	$C_{14}H_{10}O_3N_2BrCl$	235	—
31.	R_2*	$C_{14}H_{12}ONBr$	88	—
32	5-chloro-R_2	$C_{14}H_{11}ONClBr$	111	a(1.56)
33	3,5-dichloro-R_2	$C_{14}H_{10}ONCl_2Br$	109	—
34	5-bromo-R_2	$C_{14}H_{11}ONBr_2$	131	b(100)
35.	3,5-dibromo-R_2	$C_{14}H_{10}ONBr_3$	152	a(1.56)
36.	3,5-diiodo-R_2	$C_{14}H_{10}ONBrI_2$	194	—
37.	5-nitro-R_2	$C_{14}H_{11}O_3N_2Br$	205	—
38.	5-chloro-3-nitro-R_2	$C_{14}H_{10}O_3N_2BrCl$	238	—
39.	R_3*	$C_{14}H_{12}ONBr$	72	—
40.	5-chloro-R_3	$C_{14}H_{11}ONClBr$	132	—
41.	3,5-dichloro-R_3	$C_{14}H_{10}ONCl_2Br$	128	—
42	5-bromo-R_3	$C_{14}H_{11}ONBr_2$	1 8	b(25)
43.	3,5-dibromo-R_3	$C_{14}H_{10}ONBr_3$	161	—
44.	3,5-diiodo-R_3	$C_{14}H_{10}ONBrI_2$	196	—
45.	5-nitro-R_3	$C_{14}H_{11}O_3N_2Br$	216	—
46	5-chloro-3-nitro R_3	$C_{14}H_{10}O_3N_2BrCl$	228	—

R_1* 2-hydroxy-benzal-(4-bromo 2-methyl)-aniline,
R_2* 2-hydroxy-benzal-(4-bromo-3-methyl)-aniline,
R_3* 2-hydroxy-benzal-(2-bromo-4-methyl)-aniline,
b=*T. mentagophytes*.

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Synthesis of N-Benzoyl-N′-2-(4-Aryl-5-Arylazothiazolyl) Thiocarbamides as Potential Antineoplastics

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Various N-benzoyl-N′-2-(4-aryl-5-arylazothiazolyl) thiocarbamides were prepared by condensing 2-amino-4-aryl-5-arylazothiazoles with benzoyl isothiocyanate. These thiocarbamides were tested for their antineoplastic activity.

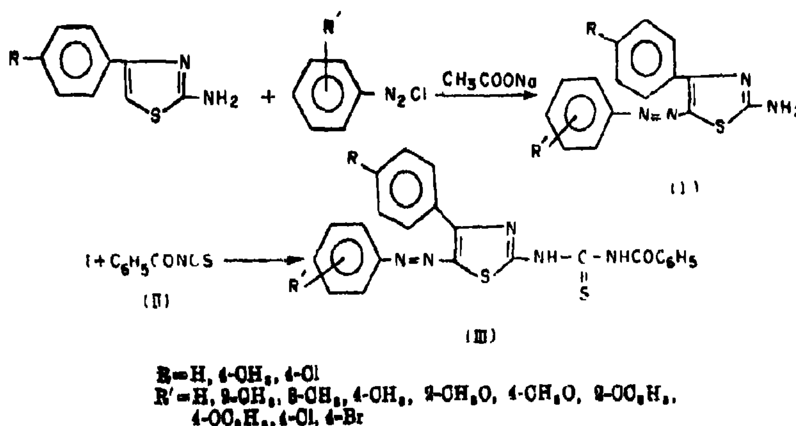
THERE has been growing interest during the last few years in compounds containing the $\overset{*}{N}-\overset{*}{N}-\overset{*}{S}$ or $\overset{*}{O}-\overset{*}{N}-\overset{*}{S}$ tridendate ligand system[1-5] or arylazo grouping[6,7]. This interest stems mainly from certain interesting carcinostatic activities of heterocyclic carboxyaldehydes, thiosemicarbazones and interfering action of 5-arylazopyrimidines with nucleic acid synthesis. Moreover, various Schiff's bases from benzaldehyde, nitrogen mustard and thiazole-amine have been reported to possess antitumour activity[8-10]. As a part of general study directed towards the development of antineoplastics, Sharma *et al*[11] synthesised and studied the properties of a series of compounds having the mixed structure. They prepared some new potential antineoplastics viz. N-phenyl-N′-2-(4-phenyl-5-arylazothiazolyl) thiocarbamides having $\overset{*}{N}-\overset{*}{N}-\overset{*}{S}$ ligand, arylazo grouping and a modified azomethine linkage. Keeping the above facts in view various N-benzoyl-N′-2-(4-aryl-5-arylazothiazolyl) thiocarbamides (III) (Table 2) were prepared by condensing 2-amino-4-aryl-5-arylazothiazoles (I) with benzoyl isothiocyanate (II)[12,13].

2-Amino-4-aryl-5-arylazothiazoles (Table 1) required in this synthesis were prepared by coupling diazotised arylamines with 2-amino-4-arylthiazoles. The latter have been obtained by the reaction of substituted acetophenones with thiourea and iodine following the procedure of Dodson and King[14].

Experimental

Preparation of 2-amino-4-aryl thiazoles[14] : Iodine (0.2 mol) was added to a slurry consisting of acetophenone (0.2 mol) and thiourea (0.4 mol). The reaction mixture was heated overnight on a steam bath. The mixture was cooled and washed with solvent ether. It was then diluted with water, heated until most of the solid had gone into solution and filtered. The filtrate was cooled and made alkaline with liquor ammonia. The 2-amino-4-arylthiazoles were precipitated which were recrystallised from dilute alcohol.

Preparation of 2-amino-4-aryl-5-arylazothiazoles[11]. Arylamine (0.02 mol) was dissolved in 3 *N* HCl and cooled to 0°. Sodium nitrite (1.4 g; 0.02 mol) dissolved in water (25 ml) was added slowly. The diazonium salt solution was filtered to a well



R=H, 4-CH$_3$, 4-Cl
R′=H, 2-CH$_3$, 3-CH$_3$, 4-CH$_3$, 2-CH$_3$O, 4-CH$_3$O, 2-C$_2$H$_5$, 4-C$_2$H$_5$, 4-Cl, 4-Br

Fig. 1

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TABLE 1—2-AMINO-4-ARYL-5-ARYLAZOTHIAZOLES (I) OBTAINED BY THE COUPLING OF ARYLDIAZONIUM CHLORIDE WITH 2-AMINO-4-ARYLTHIAZOLES

Sl. No.	R′	R=H		R=CH_3		R=Cl	
		m.p. °C	Yield%	m.p. °C	Yield%	m.p. °C	Yield%
1.	H	193-194	80	190	77	235-236	79
2.	2-CH_3	160-161	82	205-206	75.6	212-213	80.1
3.	3-CH_3	167	82.5	172-173	77.2	219-220	79.2
4.	4-CH_3	175	81	209-210	78.2	248	78.8
5.	2-OCH_3	210-211	80.8	201-202	79	140-141	80.6
6.	4-OCH_3	168-169	81.2	185	80.6	D	81
7.	2-OC_2H_5	205-206	82.6	217-218	76.8	165-167	78.2
8.	4-OC_2H_5	D	83	203-204	75	210-211	78.6
9.	4-Cl	193	78	229	79.6	238-239	76
10.	4-Br	206-207	77.5	D	80.1	D	77.2

TABLE 2—N-BENZOYL-N′-2-(4-ARYL-5-ARYLAZOTHIAZOLYL) THIOCARBAMIDES (III) OBTAINED FROM I AND II

Sl. No.	R′	R=H		R=CH_3		R=Cl	
		m.p. °C	Yield%	m.p. °C	Yield%	m.p. °C	Yield%
1.	H	217	70	181-182	71.5	219	66
2.	2-CH_3	179-180	69.2	197-198	69.2	182-184	62.5
3.	3-CH_3	155-156	66.2	148-149	70.2	193	61
4.	4-CH_3	197-198	68	175	68	193-194	63
5.	2-OCH_3	203-205	66	185-187	67	177-179	65
6.	4-OCH_3	175	66.5	144-146	67.2	247-248	65.8
7.	2-OC_2H_5	225-226	67	165-166	64.2	201-202	62
8.	4-OC_2H_5	239-240	66.2	209-210	64.8	195-196	60.1
9.	4-Cl	248	67.2	196	69.7	167-169	63.5
10	4-Br	231	67.6	223-225	68.2	239-240	60.8

cooled solution of 2-amino-4-arylthiazoles (0.02 mol) and sodium acetate (5 g) in ethanol (50 ml). After 2 hr 2-amino-4-aryl-5-arylazothiazoles were filtered and washed with water and recrystallised from DMF/ethanol.

Preparation of benzoyl isothiocyanate[12,13] Ammonium thiocyanate (5 g) was dissolved in acetone (50 ml). Benzoyl chloride (2 ml) was added. The contents were heated on a water bath at a temperature of 60-70°. The solution was filtered to remove ammonium chloride and benzoyl isothiocyanate was obtained. Yield 60%. Liquid b_{14} 133-137°, b_{10} 119°. Found: C, 58.87; N, 8.58; S, 19.65. Calcd: C, 58.82; N, 8.57; S, 19.60%.

Preparation of N-benzoyl-N′-2-(4-aryl-5-arylazothiazolyl) thiocarbamides: A mixture of benzoylisothiocyanate (1.63 g; 0.01 mol) and 2-amino-4-aryl-5-arylazothiazole (0.01 mol) in benzene (20 ml) was refluxed for 4-5 hr on a steam bath. The solvent was removed and the residue was treated with petroleum ether (40-60) and then with solvent ether. The crystalline thiocarbamide so obtained was recrystallised from DMF/alcohol.

The ir spectrum of N-benzoyl-N′-2-(4-phenyl-5-phenylazothiazolyl) thiocarbamide so prepared shows absorption due to stretching frequencies of C=S group in the region of 1370 cm^{-1}, C=O group in the region of 1690 cm^{-1} and –N=N– group in the region of 1610 cm^{-1}. Absorption due to stretching frequencies of thiazole nucleus lie in the region of 1585, 1470, 1340, 1020 and 810 cm^{-1}.

The purity of these compounds has been checked by tlc in benzene-ethylacetate mixture. All the new compounds prepared in this investigation were analysed satisfactorily for N and S.

Biological activity: Almost all the thiocarbamides tabulated in Table 2 were tested for their cytostatic and cytopathic activity in duck embryo fibroblast cell culture (in unstained preparation).

The compounds No. 2 and 5 (R=H) and 7 (R=Cl) in Table 2 have shown cytostatic activity[1]; the compounds No. 1 (R=H), 4 and 5 (R=CH_3) have shown cytopathic activity; the compounds No. 4, 8 and 10 (R=H), 2 and 10 (R=CH_3) caused individual cell rounding. The other compounds did not show any effect.

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Studies in the Cycloheptane Series. Part—XXXI : Friedel-Crafts Reaction of the Anhydride of αα-Dimethylglutaric Acid with Different Aromatic Hydrocarbons and Synthesis of 1,1-Dimethyl-3,4-benzo / substituted benzocycloheptanes and 1,1-Dimethylthieno [3,4-b] cycloheptane

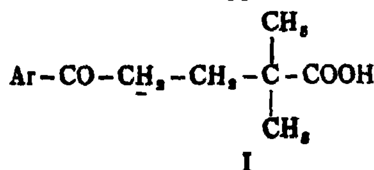
R. K. GAUTAM, S. KANNAN and G. S. SAHARIA

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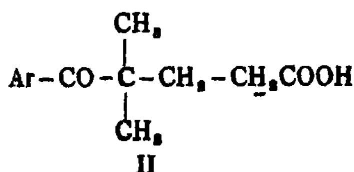
Manuscript received 6 July 1981, accepted 10 December 1981

The anhydride of αα-dimethylglutaric acid on condensation with benzene, toluene, isomeric xylenes, chlorobenzene, anisole, tetralin, naphthalene and thiophene under F. C. conditions gives the respective αα-dimethyl-γ-aroyl-n-butyric acids which on Clemmensen reduction yield δ-aryl-n-valeric acids. These on cyclisation with PPA furnish III and IV (X=O) which on Clemmensen reduction give the respective hydrocarbons (III and IV : X=H$_2$)

FRIEDEL-Crafts reaction involving the anhydride of ββ-disubstituted glutaric acids[1] has been extensively studied but similar reaction using substitution in the α-position has hardly been reported To study the behaviour of the opening of such an anhydride, αα-dimethylglutaric acid[2] [NMR-(CDCl$_3$): 1.2 δ (6H, s, CH$_3$) ; 1 8 δ (2H, t, CH$_2$ β to COOH) ; 2.4 δ (2H, t, CH$_2$COOH) ; 11 6 δ (2H, s, COOH)] has been prepared by simultaneous oxidation and hydrolysis of 4-cyano-2,2-dimethylbutyraldehyde [NMR(CDCl$_3$) · 1.1 δ (6H, s, CH$_3$), 1.9 δ (2H, t, CH$_2$ β to CN), 2 3 δ (2H, t, CH$_2$CN), 9.8 δ (1H, s, CHO)] and its anhydride condensed with different aromatic substrates to give αα-dimethyl-γ-aroyl-n-butyric acids (I). Structures were confirmed by NaOBr oxidation to known aromatic acids, uv (footnote to Table 1) and ir (two >C=O absorptions in the range 1720-1670 cm^{-1}) spectral studies. The possibility of the formation of the keto-acid (II) was ruled out on the basis of the work of Rothestein[3], according to which it was not possible to get a keto-acid from the anhydride or acid chloride derived from the tertiary acids. Additional support was lent by the

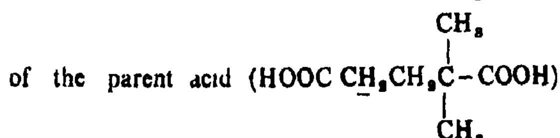


I



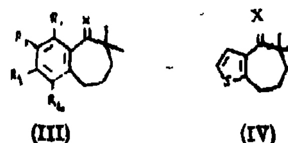
II

nmr spectra of the keto-acids. The nmr spectrum of the parent acid (HOOC CH$_2$CH$_2$C(CH$_3$)$_2$-COOH)



showed CH$_2$COOH signal at 2.4 δ, whereas CH$_2$-CO in the keto-acids (I) (footnote Table 1) appeared in the range 2 97-3.1 δ showing a considerable downfield shift. Furthermore, 2,4-DNPs of the keto-acids in this case were formed readily and in very good yields in comparison to those obtained from ββ-dimethylglutaric acid anhydrides and this might be due to the steric effect in the latter.

The keto-acids on Clemmensen reduction gave the corresponding αα-dimethyl-δ-aryl-n-valeric acids which on cyclisation with PPA furnished the corresponding cyclic ketones (III and IV : X=O) and these on reduction finally gave the corresponding hydrocarbons (III and IV · X=H$_2$).



(III) (IV)

Experimental,

αα-Dimethyl-γ-aroyl-n-butyric acid : αα-Dimethylglutaric acid anhydride (0.03 mol) on condensation with dry hydrocarbon (30 ml) in the presence of anhydrous AlCl$_3$ (0.06 mol) at 0-5° and working up in the customary manner gave the keto-acid in 80-85% yield.

TABLE 1—αα-DIMETHYL-γ-AROYL-n-BUTYRIC ACIDS

Sl. No	Aroyl	m.p. °C/ b.p. °C/mm	n_D^{33}	2,4-DNP, m.p. °C
1.	Benzoyl[a]	185/8	1.5144	191
2	4-Methylbenzoyl	85	—	215
3	3,4-Dimethylbenzoyl	72	—	193
4	2,4-Dimethylbenzoyl	156/2	1.5213	240
5	2,5-Dimethylbenzoyl	155/8	1.5432	148
6.	4-Methoxybenzoyl[b]	90	—	160
7	4-Chlorobenzoyl	150/7	1.5883	201
8.	1-Naphthoyl[c]	108	—	252
9	5,6,7,8-Tetrahydro-2-naphthoyl[d]	140/3	1.5214	202
10	2-Thenoyl[e]	191	—	249

a : λ_{max} 240 nm (ϵ 248*), b : λ_{max} 270 nm (276 5*), ^{1}H nmr ($CDCl_3$) : 1 8 δ (6H, s, CH_3), 2 0 δ (2H, t, $\underline{CH_2}-CH_2CO-$), 2.97 δ (2H, t, $\underline{CH_2}CO$), 3 85 δ (3H, s, OCH_3), 6 9 δ (2H, d, Ar protons) 11.5 δ (1H s, COOH), c. λ_{max} 245 nm (ϵ_{max} 46510), nmr ($CDCl_3$ + TFA) : 1.3 δ (6H, s, CH_3), 2.1 δ (2H, t, $\underline{CH_2}-CH_2CO-$), 3 1 δ (2H, t, CH_2CO), 7 2-8.2 δ (7H, b, m, Ar protons), d : λ_{max} 260 nm (248*), e : λ_{max} 260 nm (260*) ; (ϵ 10040), nmr ($CDCl_3$ + TFA) : 1.3 δ (6H, s, CH_3), 2 0 δ (2H, t, CH_2CH_2>C=O), 3 0 δ (2H, t, CH_2CO) ; 7.1-7 8 δ (3H, b, m, Ar protons).

All the λ_{max} values are in ethanol.

* These λ_{max} values correspond to the parent acetophenones

TABLE 2—αα-DIMETHYL-δ-ARYL-n-VALERIC ACIDS

Sl No	Aryl	b.p °C/m	n_D^{33}	S-Benzyl-isothiuronium salt, m.p. °C
1	Phenyl	145/3	1 5124	140
2.	4-Methylphenyl	140/10⁻¹	1.5014	104
3	3,4-Dimethylphenyl	165/8	1.5014	118
4.	2,4-Dimethylphenyl	132/1	1.5043	126
5	2,5-Dimethylphenyl	200/7	1.5114	106
6.	4-Methoxyphenyl	182/0 5	1.5165	119
7.	4-Chlorophenyl	156/5	1 5284	148
8	1-Naphthoyl	132/10⁻¹	1.5231	130
9	5,6,7,8-Tetrahydro-2-naphthoyl	180/8	1.5818	122
10	2-Thenoyl	180/5	1 4865	127

TABLE 3—1,1-DIMETHYL-3,4-BENZO/SUBSTITUTED BENZOCYCLOHEPTAN-2-ONES

Sl. No.	Substituent	b.p. °C/mm	n_D^{33}	2,4-DNP, m.p. °C
1.	$R_1=R_2=R_3=R_4=H$	125/1	1.5174	152
2.	$R_1=R_3=R_4=H$, $R_2=CH_3$	185/8	1.5214	230
3.	$R_2=R_4=H$, $R_1=R_3=CH_3$	110/10⁻²	1.5808	211
4.	$R_1=R_3=H$, $R_2=R_4=CH_3$	99/3	1.5845	144
5.	$R_2=R_3=H$, $R_1=R_4=CH_3$	148/3	1.5334	126
6	$R_1=R_3=R_4=H$, $R_2=OCH_3$	110/1	1.5403	214
7.	$R_1=R_3=R_4=H$, $R_2=Cl$	114/10⁻¹	1.4945	232
8.	$R_1=R_2=H$, $R_3R_4=$ (benzo)	137/10⁻¹	1.5984	191
9.	$R_3=R_4=H$; $R_1R_2=(CH_2)_4$[a]	128/1	1.5668	156
10.	Thieno [3,4-b][b]	112/10⁻²	1.4748	160

a : λ_{max} 255 nm (EtOH) ; b : λ_{max} 255 nm (EtOH)

TABLE 4—1,1-DIMETHYL-3,4-BENZO/SUBSTITUTED BENZOCYCLOHEPTANES

Sl. No.	Substitnent	b.p. °C/mm	n_D^{33}
1.	$R_1=R_2=R_3=R_4=H$	140/10⁻¹	1.5404
2.	$R_1=R_3=R_4=H$, $R_2=CH_3$	132/10⁻¹	1 4552
3	$R_2=R_4=H$, $R_1=R_3=CH_3$	98/3	1.5378
4.	$R_1=R_3=H$, $R_2=R_4=CH_3$	125/1	1.5244
5.	$R_2=R_3=H$, $R_1=R_4=CH_3$	174/10⁻¹	1 5323
6.	$R_1=R_3=R_4=H$, $R_2=OCH_3$	175/1	1.5315
7.	$R_1=R_3=R_4=H$, $R_2=Cl$	95/10⁻¹	1 4014
8	$R_1=R_2=H$ $R_3R_4=$ (benzo)	155/10⁻²	1.5814
9	$R_3=R_4=H$, $R_1R_2-(CH_2)_4$	135/10⁻²	1.5583
10.	Thieno [3,4-b]	140/1	1.5444

*αα-Dimethyl-δ-aryl-*n*-valeric acid* : The above keto-acid (0.015 mol) was reduced with Zn/Hg (40 g) and conc. HCl (100 ml), (60 hr) ; conc. HCl (5 ml) being added after every 6 hr. On normal work up, the reduced acid was obtained.

1, 1-Dimethyl-3,4-benzo/substituted benzocycloheptan-2-one : The above acid (0.009 mol) was heated with PPA (15 g P_2O_5 in 10 ml H_3PO_4) at 180-90° for 2 hr and the reaction mixture on working up gave III (X=O) or IV (X=O) in 55-60% yield.

1, 1-Dimethyl-3, 4-benzo/substituted benzocycloheptane : The cyclic ketone (0.004 mol) was reduced with Zn/Hg (20 g) and conc. HCl (60 ml) (60 hr). Conc. HCl (5 ml) was added after every 6 hr and on working up, the reaction mixture gave III ($X=H_2$) or IV ($X=H_2$).

The different products obtained above are shown in Tables 1 to 4. All the compounds in the tables gave satisfactory C and H analysis.

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Studies on the Amine Exchange Reactions in C-Mannich Bases

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Amine exchange reactions are extended to C-Mannich bases derived from 6-methoxy-1-tetralone and the reaction intermediate during exchange reaction was isolated and characterised.

AMINE exchange reactions have been utilized in C-alkylation[1,2], cyclisation of certain compounds[3-6], and in the synthesis of such Mannich bases[7], which could not be prepared by direct condensation. Usually the primary aromatic amines do not give Mannich bases on direct condensation, while they can be obtained by the exchange reactions. Blicke and Burckalter[8] could not prepare the Mannich bases from acetophenone, formaldehyde and aniline hydrochloride, but the product β-arylaminoketone was easily obtained by Craig *et al*[9], using the amine exchange reactions between β-diethylaminoketone and aniline.

Mannich bases[10] from 6-methoxy-1-tetralone (**1**)[11] were prepared with aliphatic secondary amines and with alicyclic secondary amines by the usual Mannich reaction. However, the Mannich bases from **1** with primary arylamines (*p*-chloroaniline/*p*-toluidine) could not be prepared by direct condensation of **1** with paraformaldehyde and amines.

2-Dimethylaminomethyl-6-methoxy-1-tetralone (**2**) was converted to its methiodide (**9**) on refluxing with methyl iodide in absolute alcohol. When the methiodide (**9**) in ethanol was refluxed with piperidine and sodium carbonate, the naphthalenone (**5**) was isolated as its hydrochloride. The Mannich base (**4**) was obtained by the amine exchange reaction, when the methiodide (**9**) was refluxed with morpholine and potassium carbonate in ethanol

The methiodide (**9**) also underwent amine exchange reaction with *p*-chloroaniline in ethanol in the presence of potassium carbonate yielding the product **10** which could not be obtained by direct condensation of **1** with paraformaldehyde and *p*-chloroaniline.

Evolution of trimethylamine during the exchange reaction of 2-dimethylaminomethyl-6-methoxy-1-tetralone methiodide (**9**) indicated that the intermediate in this reaction would be 2-methylene-6-methoxy-1-tetralone (**11**). Methiodide (**9**) was heated under reflux with aqueous potassium carbonate in ethanol, which resulted in the Hofmann elimination of methiodide (**9**) and evolution of trimethylamine. The isolated product, highly unstable, was completely characterized with the help of its ir, uv and nmr spectra and was identified to be the tetralone (**11**).

Since the Mannich bases of **1** with *p*-toluidine could not be obtained by direct condensation, methiodide (**9**) was subjected to exchange reaction with *p*-toluidine and the product 2-(4-methylanilinomethyl)-6-methoxy-1-tetralone (**12**) was isolated as its hydrochloride. Compound (**2**) was also subjected to amine exchange reactions with morpholine, piperidine, *p*-chloroaniline and *p*-toluidine and the exchange reactions were successful.

Experimental

Melting points were taken in open capillary tubes and are uncorrected The ir spectra were taken in a Perkin-Elmer spectrophotometer in KBr pellets. The ir spectra of the Mannich bases showed the presence of C=O bands as strong peaks in the region of 1640-1670 cm^{-1} and $-OCH_3$ bands in the region of 1140-1160 cm^{-1}.

2-Substituted aminomethyl-6-methoxy-1-tetralone hydrochloride

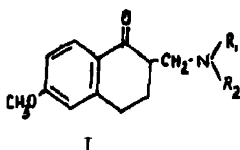
Method A A mixture of **1** (0.01 mole), paraformaldehyde (0 02 mole), amine hydrochloride (0 01 mole) and isopropyl alcohol (25 ml) was refluxed on a steam bath for 10-15 hr The reaction mixture was then concentrated under vacuum and cooled The separated product was filtered and recrystallized from appropriate solvent.

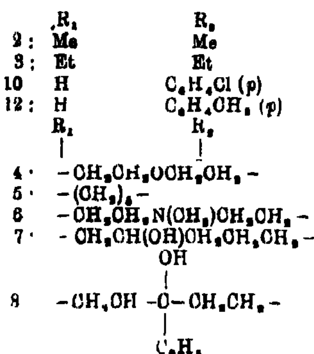
Method B · A mixture of **1** (0.01 mole), paraformaldehyde (0.02 mole), amine (0.01 mole), conc. hydrochloride acid (0.1 ml) in isopropyl alcohol (25 ml) was heated under reflux for 10-15 hr. The reaction mixture was then concentrated under vacuum and cooled. Dry HCl gas was passed into the reaction mixture at 0°. The separated product was filtered and recrystallized from appropriate solvent.

Compounds (**I**) prepared according to these two methods are presented along with relevant data in Table 1.

TABLE 1

Sl. No.	R_1	R_2	Method	Melting point °C	Yield %	Crystallisation solvent	% Nitrogen Found	% Nitrogen Calcd.
2.	Me	Me	A	164	55 7	Isopropyl alcohol	5 10	5.19
3.	Et	Et	A	186	40	Ethanol	4.68	4.70
	R_1—R_2							
4.	$-CH_2CH_2OCH_2CH_2-$		B	168-70	54 4	Ethanol	4 80	4.49
5.	$-(CH_2)_5-$		B	182	68	Isopropyl alcohol	4.36	4.82
6.	$-CH_2CH_2N(CH_3)CH_2CH_2-$		B	162	40	Methanol	8.68	8.62
7.	$-CH_2CH(OH)CH_2CH_2CH_2-$		B	176	41	Ethanol	4 17	4.30
8.	$-CH_2CH-C(OH)(C_6H_5)-CH_2CH_2-$		B	166	88	Ethanol	3.40	3 46





2-Dimethylaminomethyl-6-methoxy-1-tetralone methiodide (9) · A mixture of 2-dimethylaminomethyl-6-methoxy-1-tetralone hydrochloride (2.70 g ; 0.01 mole), methyl iodide (6 g ; 0.04 mole) and absolute ethanol (20 ml) was refluxed gently for 4 hr Excess of methyl iodide was removed and the solid mass, separated on cooling, was filtered and recrystallized from absolute ethanol. Yield 2.70 g (72%), m.p. 151-152°. NMR ($CDCl_3$). δ 2.1-2.4 [$-CH_2-N$, broad multiplet], δ 2.50-2.70 [2H, quartet (4-CH_2)], δ 3.05 [9H, each singlet, $-N(CH_3)$], δ 3.30-3.70 [3H multiplet, (3-CH_2 and 2-CH)], δ 3.95 [3H, singlet, (6-OCH_3)], δ 6.75-7.1 [2H, complex quartet, (7-CH and 8-CH aromatic)], δ 7.8-8.1 (1H, complex quartet, (5-CH aromatic)]. M. wt. 375 ; Analysis · Nitrogen ; Found : 3.69%. Calcd. : 3.73%.

2-Substituted aminomethyl-6-methoxy-1-tetralone hydrochloride by the exchange reaction of **9** *with amine* 2-Dimethylaminomethyl-6-methoxy-1-tetralone methiodide/hydrochloride (0.005 mole) was dissolved in aq. ethanol (50% ; 25 ml). To this were added amine (0.005 mole) and potassium carbonate (0.7 g ; 0.005 mole). The reaction mixture was heated under reflux for 4 hr. Solvent was removed from the reaction mixture and water (25 ml) was added. The separated oil was extracted with ether, the ether layer was distillled and the remaining semi-solid mass was dissolved in dry benzene (25 ml). Dry HCl gas was passed into the benzene solution, cooled to 0°. The separated solid product (I) was filtered and washed with dry benzene and recrystallized from appropriate solvent.

(Analytical data—vide Tables 2A and 2B).

2-Methylene-6-methoxy-3,4-dihydro-1 (2)-naphthalenone(11) 2-Dimethylaminomethyl-6-methoxy-3, 4-dihydro-1-(2) naphthalenone methiodide (1.9 g ; 0 005 mole) was dissolved in aqueous ethanol (50% ; 50 ml). To this potassium carbonate

TABLE 2A—WHEN EXCHANGE IS CARRIED OUT WITH THE COMPOUND (9)

Amine to be added	No. of Comp. obtained	Melting point °C	Yield %	Crystallisation solvent	% Nitrogen Found	% Nitrogen Calcd
Morpholine	4	170	70	Ethanol	4.47	4.49
Piperidine	5	181	82	Isopropyl alcohol	4.50	4.52
p-Chloroaniline	10	206-7	40	Methanol	3.82	3 98
p-Toluidine	12	176	52	Ethanol	4.15	4.22

TABLE 2B—WHEN EXCHANGE IS CARRIED OUT WITH THE COMPOUND (2)

Amine to be added	No of the Comp. obtained	Melting point °C	Yield %	Crystallisation solvent	% Nitrogen Found	% Nitrogen Calcd.
Morpholine	4	169	63	Ethanol	4.34	4.49
Piperidine	5	180-81	71 5	Isopropyl alcohol	4.41	4.52
p-Chloroaniline	10	206	45	Methanol	3.92	3.98
p-Toluidine	12	177	86	Ethanol	4.09	4.22

(1.4 g ; 0.01 mole) was added and heated under reflux for 6 hr. The reaction mixture was concentrated in vacuum and water (30 ml) was added. It was then extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulphate. Ether was then removed completely and the residue was recrystallized from absolute ethanol. The product (11) was further purified by preparative layer chromatography, by dissolving in acetone and using benzene/ethyl acetate (2%), solvent mixture. Yield 0.50 g (53.2%), m.p. 121°. IR 1660 (C=C exocyclic and C=O) ; UV ($CHCl_3$) λ_{max} 280 (ϵ-12,600) ; NMR ($CDCl_3$) δ 2.05-2.50 [4H, complex quartet, (3-CH_2 and 4-CH_2) skeleton], δ 3.85 [3H, singlet, (6-OCH_3)], δ 6.45-6.80 [2H, quartet (=CH_2)], δ 7.15-7.40 [2H, complex quartet (7-H and 8-CH)] δ 7.88-8.10 [1H, doublet (5-CH)].

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Electron Impact Induced Fragmentation of Schiff Bases of 2-hydroxy-5-methylbenzaldehyde

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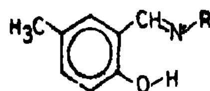
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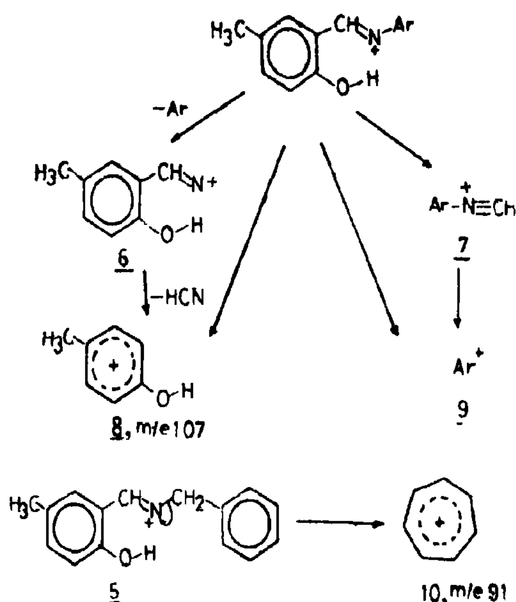
Mass spectral fragmentation of Schiff bases derived from 2-hydroxy-5-methylbenzaldehyde and arylamines as well as benzylamine are reported. Six-centre H-transfer McLafferty rearrangement, HCN elimination from M$^{+\cdot}$ as well as from the other fragments and formation of a benzisoxazole cation are the common features of the mass spectra. Arylamines Schiff bases show M$^{+\cdot}$ as the base peaks while benzylamine Schiff base gives m/e 91, tropylium ion, as the base peak.

MASS spectral studies of Schiff bases have not been reported before 1966. Since then also, the subject has not been thoroughly investigated; particularly Schiff bases of 2-hydroxyarylaldehydes have not been given due attention. *ortho*-Substituent is known to exert a profound effect on the mode of fragmentation of aromatic compounds. In light of these facts, in course of our studies on Schiff bases, it was considered interesting to study the mass spectral fragmentation of a few Schiff bases of 2-hydroxy-5-methylbenzaldehyde[1-9].

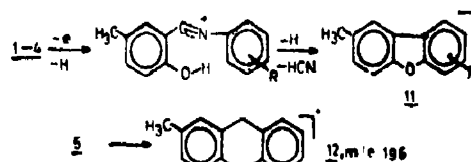
Initial ionization always occured on the N-atom giving imminium ion. Parallel to the ordinary Schiff bases[1], these compounds gave stable molecular ions (M$^{+\cdot}$) and the M$^{+\cdot}$ was the base peak in the spectra when the anils were derived from aromatic amines (i.e 1-4). Benzylamine Schiff base 5, gave an intense M$^{+\cdot}$ peak but it was not the base peak. The base peak was at m/e 91, which corresponded to tropylium ion[10] formed by α-cleavage. The unusual stability and facility of the formation of this ion might be the reason of the high intensity of this peak. Compounds 1-4 were observed to cleave at either end of the azomethine (–CH=N–) linkage to give major fragments (6 and 7) which decomposed further by the ejection of HCN to daughter ions (8 and 9). These second generation ions can also be formed directly from the molecular ions (Scheme 1). 2 showed some diversion due to 4-CH_3 group. It also gave significant tropylium ion at m/e 91, which was formed from the ion 7 formed through α-cleavage (7-10). The peak at m/e 91 was second in intensity to the base peak M$^{+\cdot}$. Stability of the molecular ions was also reflected in the



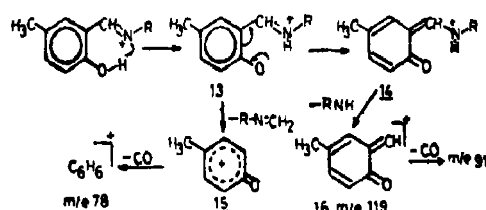
1 : R = –Ph
2 : R = –C_6H_4-4-CH_3
3 : R = –C_6H_4-4-OCH_3
4 : R = –C_6H_4-4-NO_2
5 : R = –CH_2–C_6H_5



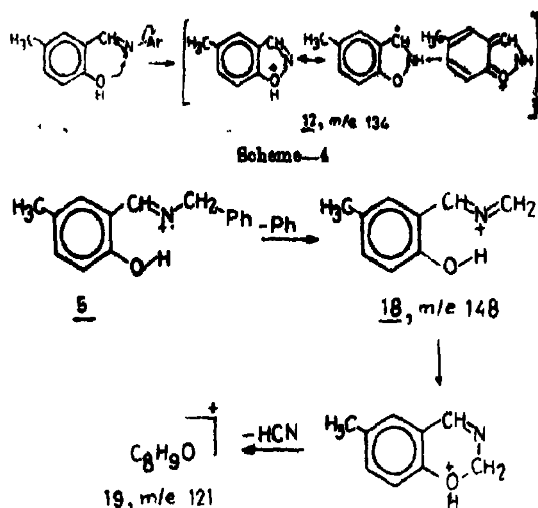
Scheme—1



Scheme—2



Scheme—3



observation that from the ions substituents on the N-phenyl moiety either were ejected as such or ejected as typical neutral particles from them, e.g. **3** showed ($M-OCH_3$) and ($M-CHO$) peaks, while, **4** showed ($M-NO$), ($M-CO$) and ($M-NO_2$) peaks. Besides the M^+, all the compounds showed ($M-1$) peaks nearly equally strong, formed by the loss of the azomethine H[1] and ($M-2$) of low intensity. All the compounds showed ($M+1$) peaks[2] of variable intensities, probably due to the ions formed by the intermolecular H-capture by the molecular ions.

Skeletal rearrangements of the type $[ABC]^{+\cdot} \rightarrow [AC]^{+\cdot} + B$ are common features of the compounds of the type $Ar-X=Y-Ar^{3-5}$. **1-5** showed elimination of HCN ($M-HCN$) through a similar rearrangement process[6]. Participation of *ortho*-OH group was obvious in these processes and **1-4** gave a dibenzofuran ion **11** Through similar mechanism, **5** gave a dibenzopyran ion **12** at m/e 196. Another interesting case of similar participation was observed in the formation of **16** at m/e 119 and **15** at m/e 106. These ions could be formed through a six-centre H-transfer from $-OH$ to imminium ion by a McLafferty rearrangement. **15** and **16** may undergo elimination of CO to form ions m/e 78 and m/e 91, respectively. Peak at m/e 91 of variable intensity in all the spectra could thus be accounted for. The peak at m/e 134 in all the spectra was attributed to benzisoxazole ion **17** which was stabilized by resonance. **17** could be formed by the participation of the *o*-OH group in the isoxazole ring formation with concomitant loss of the N-aryl radical (Scheme 4). As benzisoxazole type ions are less stabilized than the corresponding benzoxazole ions[1], intensity of the peak at m/e 134 was never more than 50%. **5** was observed to fragment by a different route through ion **18** ($M-Ph$) to form ion at m/e 121 by the ejection of HCN.

The Schiff bases were prepared by the reaction of equimolar amounts of the appropriate amines with 2-hydroxy-5-methylbenzaldehyde. The bases were crystallized from ethanol.

The mass spectra were recorded on a Varian Mat-112 S Mass spectrometer at 70 eV energy.

Acknowledgement

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Transformation of Sucrose : An Alternative Route for Amination

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Mesylation of sucrose with 1 and 2 moles of mesylchloride (methane sulfonyl chloride) separately followed by acetylation in pyridine formed mono-, di-, tri- and tetra-O-mesyl sucrose-acetates respectively. Mono and dimesyl sucrose-acetates are converted into their amino derivatives via iodo and azido compounds in appreciable yields.

HOCKETT and ZIEF[1] reported the formation of sulfonyl esters of sucrose by reaction with mesyl or tosyl chlorides (*p*-toluenesulfonyl chloride) in pyridine solution at 0°. They recorded the analytical values for the amorphous powders of tri-O-tosyl, octa-O-tosyl and octa-O-mesyl sucrose derivatives. Lemieux and Barrette[2] carried out tri-O-tosylation of sucrose and on chromatographic analysis of the mixture formed they obtained di-, tri-, tetra- and penta-O-tosyl-sucroses in 1 : 1 : 0.33 : 0.5 molar ratios respectively. Issacs and coworkers[3] prepared 1'-6-6' tri-O-tosyl sucrose pentaacetate and confirmed its structure by converting it into 1', 4 : 3, 6 : 3', 6' tri anhydrosucrose by treating it with sodium methoxide in methanol.

Khan[4] confirmed the findings of Issacs and coworkers by preparing the 1',4 : 3, 6 : 3', 6' tri anhydrosucrose from 1'-6-6' tri-O-tosyl sucrose and its benzoate derivatives by treating with sodium methoxide in methanol.

A large number of nucleophilic substitution reaction on sulfonyl esters of sucrose have been studied by various workers[5-9] from time to time. In the present work the preparation of mono- and di-mesyl sucrose acetates by mesylation of sucrose (1 mole) with mesylchloride (1 and 2 moles separately) in pyridine followed by acetylation with acetic anhydride in the same solution has been carried out to study the reactivities of –OH groups of sucrose. Products obtained on nucleophilic substitution with sodium iodide and sodium azide separately gave the iodo and azido derivatives of sucrose respectively.

Azido derivatives of sucrose have also been prepared in good yield and comparatively at low temperature by replacement of iodo group by azido group. Azido derivatives of sucrose on reduction with platinum oxide gave amino sucroses. This provides an alternative route for the preparation of amino sucroses to that of previous workers from the chlorodeoxy sugars[7,10-12] which required higher temperature such as 80-90° and in comparatively lower yields.

Experimental

General : All evaporations were carried out under reduced pressure below 50°. Melting points were recorded in capillary tubes and are uncorrected. Optical rotations were measured on a Bellingham-Stanley type I polarimeter in 1 dm tubes. Column chromatography on silica gel was carried out at room temperature using BDH, India (60-120 mesh) silica gel activated at 120° before use. Thin layer chromatography was performed at room temperature on silica gel G (BDH, India). The spraying reagent used was 10% solution of conc. H_2SO_4 in ethanol. NMR spectra were recorded in chloroform-d at Varian XL-100 FT NMR spectrometer with tetramethylsilane as internal standard. All the solvents used were BDH, India dried and freshly distilled before use.

Monomesylsucrose heptaacetate : Mesylchloride (1.14 ml) was added dropwise to a well stirred mixture of sucrose (5 g) and pyridine (100 ml) at 0° in 15 to 20 min. The reaction mixture was stirred for 3 hr at 0° and then allowed to stand at room temperature for 24 hr Acetic anhydride (12 ml) was added dropwise in the same reaction mixture at room temperature and the reaction mixture was kept for 24 hr. The reaction product was poured with stirring into iced water, the powdery product was filtered off, dried and dissolved in acetone Acetone solution was decolourized with activated animal charcoal, filtered and poured with stirring into iced water. White amorphous powder (7.3 g) showed on tlc, chloroform : acetone (5 : 1), a fast moving fraction (sucrose octaacetate) and four slower moving products. Product obtained (6 g) on elution from silica gel (200 g) with chloroform : acetone (7 : 1) gave following.

Mixture of 6- and 6'-mono-O-mesylsucrose heptaacetate (**1**) *:* (0.6 g, 5.8%), R_f value 0.56 (chloroform : acetone 5 : 1), m.p. 62-63°, $[\alpha]_D^{28}$+49.7° (c 2.1, chloroform) (Found :C, 45.4 ; H, 5.3 ; S, 4.1. $C_{27}H_{38}O_{20}S$ requires C, 45.3 ; H, 5.3 ; S, 4.48%).

NMR data ($CDCl_3$): τ 4.28, 4.37 (2d, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.94 (t, 1 proton $J_{4,5}$ 9.0 Hz, H-4), 5.11 (dd, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 6.88 (s, 3 protons, 1 Ms), 7.74-8.14 (m, 21 protons, 7Ac). The remaining resonances could not be interpreted due to overlapping.

6,6'-Di-O-mesylsucrose hexaacetate (**2**): (1.5 g, 13.6%), R_f value 0.46 (chloroform : acetone 5 : 1) was then eluted and isolated as a white amorphous powder, m.p. 67-68°, $[\alpha]_D^{25}+50.2°$ (c, 1.16, chloroform) (Found: C, 41.3; H, 5.0; S, 8.2. $C_{26}H_{38}O_{21}S_2$ requires C, 41.6; H, 5.0; S, 8.5%).

NMR data ($CDCl_3$): τ 4.33 (d, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.95 (t, 1 proton, $J_{4,5}$ 9.0 Hz, H-4), 5.11 (dd, 1 proton, $J_{2,3}$ 10.0 H_z, H-2), 6.8-6.96 (m, 6 protons, 2 Ms), 7.74-8 14 (m, 18 protons, 6 Ac). The remaining resonances could not be interpreted due to overlapping.

1',6,6'-Tri-O-mesylsucrose pentaacetate (**3**): (1.2 g, 10.4%), R_f value 0.36 (chloroform : acetone 5 . 1) was then eluted and isolated as a white amorphous powder, m.p. 72-73°, $[\alpha]_D^{25}+46.8°$ (c, 1.18 chloroform) (Found · C, 37.9; H, 4.8; S, 11.8. $C_{25}H_{38}O_{22}S_3$ requires C, 38.1; H, 4.83, S, 12.2%).

NMR data ($CDCl_3$): τ 4.28 (d, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.91 (t, 1 proton, $J_{4,5}$ 9.0 Hz H-4), 5.06 (dd, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 6.7-7 0 (m, 9 protons, 3 Ms), 7.62-8.12 (m, 15 protons, 5 Ac). The remaining resonances could not be interpreted due to overlapping.

1',2,6,6'-Tetra-O-mesylsucrose tetraacetate (**4**): (0.6 g, 5%), R_f value 0.26 (chloroform, acetone 5 : 1) was then eluted and isolated as a white amorphous powder, m.p. 76-77°, $[\alpha]_D^{25}+46.9°$ (c 1.05, chloroform) (Found: C, 34.9; H, 4 5; S, 15.1. $C_{24}H_{38}O_{23}S_4$ requires: C, 35.0; H, 4.6; S, 15.6%).

NMR data ($CDCl_3$): τ 4.26 (d, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 6.7-7.1 (m, 12 protons, 4 Ms), 7.7-8.1 (m, 12 protons, 4 Ac). The remaining resonances could not be interpreted due to overlapping.

Dimesylsucrose hexaacetate: Mesyl chloride (2.3 ml) was added dropwise to a well stirred mixture of sucrose (5 g) and pyridine (100 ml) at 0° in 15 to 20 min. The reaction mixture was stirred for 3 hr at 0° and then allowed to stand at room temperature for 24 hr. Acetic anhydride (25 ml) was added dropwise in the same reaction mixture at room temperature and the reaction mixture was worked up in the same way as in monomesylsucrose heptaacetate. Product obtained (8 g) on elution from silica gel (300 g) with chloroform : acetone (7 : 1) gave **1** (0.96 g, 9.2%); **2** (2 g, 18%); **3** (2 g, 17.4%) and **4** (1.36 g, 11.3%).

6- and 6'-Monoiodo-monodeoxysucrose heptaacetate (**5**): Sodium iodide (0.3 g) was added to a solution of **1** (0.5 g) in butanone (20 ml). The reaction mixture was refluxed with stirring for 6 hr when the tlc indicated that the yield of monoiodide was optimal and the reaction was stopped. Sodium methane sulfonate and unreacted sodium iodide were filtered off and washed with ice-cold butanone. The filtrate was concentrated to a syrup which was dissolved in chloroform and washed with sodium thiosulfate solution and water to remove the dissolved free iodine in the solution, dried over anhydrous sodium sulfate, filtered and concentrated to a syrup which was chromatographed on silica gel (30 g) with carbon tetrachloride : acetone (6 : 1) gave a syrup **5** (0.31 g, 60%) $[\alpha]_D^{25}+40.2°$ (c 1.12, chloroform) (Found: C, 41.4; H, 4.6; I, 16.5. $C_{26}H_{35}O_{17}I$ requires C, 41.8; H, 4.7; I, 17.02%).

6,6'-Diiodo-6,6'-dideoxysucrose hexaacetate (**6a**). *6- and 6'-monoiodo-monodeoxy-monomesylsucrose hexaacetate*, **6b**: A sample (1 g) of **2** was iodinated with sodium iodide (0.7 g) as described in the synthesis of **5**, yielded a syrup which was chromatographed on silica gel (40 g) with carbon tetrachloride : acetone (7 : 1) gave initially **6a** (0.45 g, 40%) $[\alpha]_D^{25}+26.6°$. (c 0.97, chloroform) (Found: C, 35.0; H, 3.8; I, 29.6. $C_{24}H_{32}O_{15}I_2$ requires C, 35.4; H, 3.9; I, 31.2%) and **6** (0.26 g, 25%) $[\alpha]_D^{25}+33.6°$ (c 0.7, chloroform) (Found: C, 37.9; H, 4 2; I, 15 7. $C_{25}H_{35}O_{18}SI$ requires C, 38.3; H, 4.5; I, 16.2%).

NMR data ($CDCl_3$) τ 4.23, 4.36 (2d, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.92 (t, 1 proton, $J_{4,5}$ 9.0 Hz, H-4), 5.1 (dd, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 6.5 (d, H-6 and 6') 6.85 (s, 3 protons, 1 Ms), 7.74-8.0 (m, 19 protons, 6 Ac). The remaining resonances could not be interpreted due to overlapping.

6-and 6'-Monoazido-monodeoxysucrose heptaacetate (**7**). A mixture **1** (0.5 g) and sodium azide (0.25 g) in N, N-dimethylformamide (15 ml) was heated at 85° for 30 hr under agitation. The reaction mixture was filtered and the filtrate was evaporated. The residue was acetylated with acetic anhydride in pyridine to acetylate the deacetylated groups in usual manner to a product which was chromatographed on silica gel (40 g) with carbon-tetrachloride : acetone (7 : 1) gave a glassy solid **7** (0.34 g, 74% $[\alpha]_D^{25}+56.0°$ (c 0.9, chloroform) (Found . C, 47.1; H, 5.1; N, 6.2. $C_{26}H_{35}O_{17}N_3$ requires C, 47.2; H, 5.3; N, 6.35%).

6,6'-Diazido-6,6'-dideoxysucrose hexaacetate (**8**): A mixture of **2** (0.5 g) and sodium azide (0.3 g) in N,N-dimethylformamide (15 ml) was heated at 110° for 30 hr under agitation. The mixture was filtered and the filtrate was evaporated to dryness. The residue was acetylated with acetic anhydride in pyridine as usual to a product which was chromatographed on silica gel (40 g) with carbon tetrachloride : acetone (7 : 1) gave a syrupy product **8**, (0.34 g, 82%), $[\alpha]_D^{25}+5.5°$ (c, 2.1, chloroform) (Found: C, 44.3; H, 4.7; N, 12.9. $C_{24}H_{32}O_{15}N_6$ requires 44.7; H, 4.9, N, 13.0%).

6- and 6'-Monoazido-monodeoxysucrose (**9**): A solution of **7** (0.4 g) in dry methanol (30 ml) was treated with 2 *M* methanolic sodium methoxide

(1 ml) at room temperature for 5 hr with stirring, tlc (chloroform : ethanol, 5.3) then showed one product running slower than the starting material. After neutralisation with Amberlite IR 120 (H^+) resin (freshly regenerated and washed with methanol before use), the solution was concentrated to a syrup. The syrupy residue was boiled with light petroleum which was then decanted carefully. This operation was repeated three to four times to remove all of the methyl acetate. The product was dried over phosphoric oxide and paraffin wax overnight to give the monoazide as a syrup **9** (0.2 g), 91% $[\alpha]_D$ +58.4° (c, 1.5, water) (Found : C, 38.8 ; H, 5.5 ; N, 11.1. $C_{12}H_{21}O_{10}N_3$ requires C, 39.2 ; H, 5.7 ; N, 11.4%).

6,6'-Diazido-6,6'-dideoxysucrose (**10**) : A sample of **8** (0.3 g) was deacetylated with 2*M* methanolic sodium methoxide (1 ml) as described in the synthesis of **9** gave the diazide as a syrup **10**, (0.14 g, 81%) $[\alpha]_D$ +61° (c 1.4, water) (Found : C, 36.2 ; H, 4.8 ; N, 21.1. $C_{12}H_{20}O_9N_6$ requires C, 36.7 ; H, 5.1 ; N, 21.4%).

6- and 6'-Monoamine-monodeoxysucrose (**11**) : **9** (0.15 g) was hydrogenated in 50% aqueous ethanol (50 ml) in the presence of Adam's platinum oxide (50 mg) at 3.4 Kg/cm² of hydrogen atmosphere at 35-40° for 20 hr. After the catalyst was removed, the solution was concentrated and crystallized from ethanol : methanol : water (3 : 3 : 4 v/v) in refrigerator for 20 days to give **11**, (90 mg, 70%), m. p. 137-138° (dec.) $[\alpha]_D$ +60.5° (c 0.8, water) (Found . C, 42.0 ; H, 6.4 ; N, 4.0. $C_{12}H_{23}O_{10}N$ requires C, 42.2 ; H, 6.8 ; N, 4.1%).

6,6'-Diamino-6, 6'-dideoxysucrose (**12**) : **10** (0.1 g) was hydrogenated with Adam's platinum oxide as described in the synthesis of **11**. After the catalyst was removed, the solution was concentrated and crystallized from ethanol : methanol : water (2 : 2 : 4 v/v) in a refrigerator for 20 days to give **12**, (64 mg, 80%), m.p. 126-129° (dec) $[\alpha]_D$ +63° (c 0.54, methanol) (Found : C, 42.1 ; H, 7.0 ; N, 8.1. $C_{12}H_{24}O_9N_2$ requires C, 42.3 ; H, 7.0 ; N, 8.2%).

6- and 6'-Monoazido-monodeoxysucrose hepta-acetate (**7**) *from* **5** : A mixture of **5** (0.5) and sodium azide (0.25 g) in N, N-dimethylformamide (15 ml) was stirred for 48 hr under agitation at 25°. The mixture was filtered and the filtrate on dispersing into iced water gave a white amorphous powder which was decolourized with activated animal charcoal, filtered and filtrate concentrated to a syrup which was chromatographed on silica gel (30 g) with carbon tetrachloride : acetone (7 : 1) gave a glassy solid **7**, (0.41 g, 95%), $[\alpha]_D$ +56.5° (c, 0.8, chloroform) (Found : C, 47.0 ; N, 6.1 ; H, 4.9. $C_{26}H_{35}O_{17}N_3$ requires C, 47.2 ; H, 5.3 ; N, 6.35%).

6,6'-Diazido-6, 6'-dideoxysucrose hexaacetate (**8**) *from* **6a** : A mixture of **6a** (0.4 g) and sodium azide (0.3 g) in N,N-dimethylformamide (15 ml) was stirred at 35° for 50 hr under agitation. The reaction mixture was worked up as described in the synthesis of **7** from **5** and on purification by chromatography on silica gel (30 g) carbon tetrachloride : acetone (7 : 1) gave a syrupy product **8**, (0.29 g, 94%), $[\alpha]_D$ +5.5° (c 2.0, chloroform) (Found : C, 44.1 ; H, 4.5 ; N, 12.7. $C_{24}H_{32}O_{15}N_6$ requires C, 44.7 ; H, 4.9 ; N, 13.0%).

Results and Discussion

Mesylation of sucrose (1 mole) with methanesulfonyl chloride (1 and 2 moles) in pyridine at 0° and acetylation by acetic anhydride in the same solution at room temperature gave the product which on chromatographic separation and purification gave mono-O-mesyl sucrose heptaacetate (**1**), di-O-mesylsucrose hexaacetate (**2**), tri-O-mesylsucrose pentaacetate (**3**) and tetra-O-mesyl sucrose tetraacetate (**4**). The first product **1** was a (2 : 1) mixture of 6 and 6'-mono-O-mesylsucrose heptaacetate as revealed by nmr spectrum which showed the doublets in low field (τ 4.28, 4.36) due to H-1 in the 6 and 6' mono-O-mesylsucrose heptaacetates. This showed that the reactivities of 6- and 6'-hydroxyl groups in sucrose are 0-6$\geq$0-6'. Products **2**, **3** and **4** were 6-6'-di-O-mesyl, 1'-6-6'-tri-O-mesyl and 1',2, 6, 6'-tetra-O-mesylsucrose acetates respectively as confirmed by their nmr spectra. In comparison with the ^1H nmr data for octa-O-acetylsucrose, the signals due to the protons attached to the carbon having sulfonyl groups appeared at a slightly higher fields.

The formation of products **1,2,3,4**, clearly showed that decreasing order of reactivity of different – OH groups in sucrose is as follows :



0-6>0-6'>0-1'>0-2.

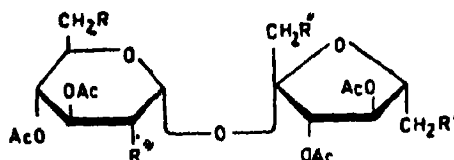


Fig. 1

(1). R=OMs , R'=R''=R'''=OAc
R'=OMs , R=R''=R'''=OAc
(2). R=R'=OMs , R''=R'''=OAc
(3) R=R'=R''=OMs , R'''=OAc
(4) R=R'=R'=R'''=OMs
(5). R=I, R'=R''=R'''=OAc
R'=I , R'=R''=R'''=OAc
(6a). R=R'=I,
R''=R'''=OAc
(6b). R=I, R'=OMs ,
R''=R'''=OAc
(7). R=N₃ ,
R'=R''=R'''=OAc
R'=N₃
R=R''=R'''=OAc
(8). R=R'=N₃ ,
R''=R'''=OAc

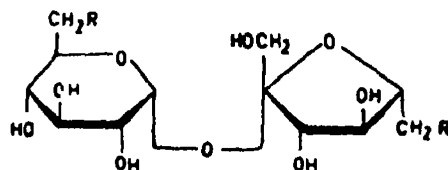


Fig. 2

(9). R=N₃ , R'=OH
R'=N₃ , R=OH
(10). R=R'=N₃
(11). R=NH₂ ; R'=OH
R'=NH₂ ; R=OH
(12). R=R'=NH₂

Investigation of the reaction of **1** with sodium iodide in butanone gave the mixture of 6- and 6'-mono-iodo-monodeoxysucrose heptaacetate (**5**). Similarly reaction of **2** with sodium iodide in butanone gave 6,6'-diiodo-6,6-dideoxysucrose hexaacetate (**6a**) and 6- and 6'-monoiodo-monodeoxy-monomesylsucrose hexaacetate (**6b**).

6b was a (3 : 1) mixture of 6- and 6'-monoiodo-monodeoxy-monomesylsucrose hexaacetate as revealed by nmr which showed two doublets in low field (τ 4.23, 4.36) and one doublet (τ 6.53) of 2 protons H-6 and H-6' (due to overlapping of two doublets of $-CH_2-I$ because of the mixture of 6 -and 6'-monoiodo-monodeoxy-monomesylsucrose hexaacetate). **1** and **2** with sodium azide in N,N-dimethylformamide gave the mixture of 6- and 6'-monoazido-monodeoxysucrose heptaacetate (**7**) and 6,6'-diazido-dideoxysucrose hexaacetate (**8**).

7 and **8** on deacetylation with 2 *M* methanolic sodium methoxide in absolute methanol gave the mixture of 6- and 6'-monoazido-monodeoxysucrose (**9**) and 6,6'-diazide-6,6'-dideoxysucrose (**10**).

9 and **10** on catalytic hydrogenation with platinum oxide (Adam's catalyst) under pressure 3.4 kg/cm^2 of hydrogen atmosphere at 35-40° for 20 hr gave the mixture of 6- and 6'-monoamino-monodeoxysucrose (**11**) and 6,6'-diamino-6,6'-dideoxysucrose (**12**).

Replacement of iodo-substituents in the 6- and 6'-monoiodo-monodeoxysucrose heptaacetate (**5**) and 6,6'-diiodo-6,6'-dideoxysucrose hexaacetate (**6a**) by azide was readily achieved in N,N-dimethylformamide to **7** and **8** in 95 and 84% yields respectively.

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Spectrophotometric Determination of Chromium in Steel by Extraction of its Ion Association Complex with Tetraphenylarsonium Chloride**

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Chromium(VI) forms ion association complex with tetraphenylarsonium chloride extractable into chloroform and 1,2-dichloroethane. Based on the ultraviolet absorption of this ion pair in 1,2-dichloroethane, the better extractant of the two, a method fo the determination of chromium was evolved. Interfering effect of a number of ions wrere investigated. The relative ease of conversion of chromium(III) to chromium(VI) affords a means of its separation from most of the commonly associated elements. Methods have also been developed to remove the interference due to a few anions that are extractable with tetraphenylarsonium chloride into 1,2-dichloroethane The method was subsequently used in the determination of chromium in standard steel samples.

SEVERAL reagents are known which are used for the determination of small amounts of chromium by the spectrophotometric method. The most sensitive reaction for determining chromium is the one between S-diphenyl carbazide and chromium(VI) in acid solution[1]. The resulting red-violet species is reported to be extractable by organic solvents like *iso*amyl alcohol[2], chloroform[3] and cyclohexanol[4] and was used in recent years for spectrophotometric determination of chromium(VI)[5-7] using prior separation methods. Other reagents used for the determination of chromium are NH_4-pyrrolidine-1-carbodithioate[8], uramildiacetic acid[9], 3-hydroxy-4-(2-hydroxy-1-naphthylazo)naphthalene-1-sulphonic acid[10] and mercaptoacetic acid[11]. Majumder and De[12], however, used 2-thenoyltrifluoroacetone(TTA) for direct spectrophotometric determination of chromium by extracting the Cr(III)-TTA complex into benzene.

It has been found, following the suggestion of Alimarin Perezhogin[13] that chromium(VI) forms ion association complex with tetraphenylarsonium cation extractable into chloroform or 1,2-dichloroethane, a fact which had been reported earlier by Hala *et al*[14]. Baishya and Heslop[15] determined chromium in aluminium alloys both by neutron activation and isotope dilution analysis based on the principle of substoichiometric extraction with tetraphenylarsonium chloride.

In the present work spectrophotometric determination of chromium by extraction of its ion pair with tetraphenylarsonium chloride into 1,2-dichloroethane was investigated. The relative ease of inter conversion of chromium(III) to chromium(VI) and formation of easily extractable Cr(VI)-TPA ion pair made it possible to determine chromium in presence of most of the commonly associated elements. The method was applied in the determination of chromium in standard steel samples.

Experimental

Apparatus : Absorbance measurements were made with a Beckman DK-2 spectrophotometer

Reagent : A 0.01 *M* solution of tetraphenylarsonium chloride (Fluka A.G., Buchs S.G.) in distilled water was employed as the reagent.

Standard solution : 0.3734 g of potassium chromate (AnalaR) was dissolved in 1 *N* H_2SO_4 in a 100 ml standard flask and the volume was made up with the same acid. The resulting solution contained 0.0001 g of chromium per ml and was used as a stock solution. Solutions of lower concentrations were prepared from the stock solution by dilution with 1 *N* H_2SO_4.

Other compounds used for studying interferences were ferric ammonium sulphate, cadmium sulphate, copper sulphate, mercuric chloride, ammonium molybdate, sodium tungstate, potassium permanganate, potassium thiocyanate, ammonium fluoride, sodium oxalate, sodium vanadate, sodium perchlorate and potassium antimonyl tartrate.

Procedure for calibration : An aliquot of the standard solution containing 50 μg to 200 μg of chromium was taken in several different separating funnels. The volume in each was made 5 ml by adding 1 *N* H_2SO_4. To each of these solutions was then added 1 ml of 0.01 *M* tetraphenylarsonium chloride reagent. The resulting mixture was then shaken for 2 min with 5 ml of 1,2-dichloroethane. The organic layer was separated and the absorbance was measured at 363 nm against the pure solvent. A plot of these absorbance values against concentration gave a straight line indicating that Beer's law

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is obeyed over the concentration range 10 to 40 μg of chromium per ml of the organic phase.

The process was repeated in a few more aliquots taken at random and the amount of chromium calculated from the calibration curve showed good recovery of chromium with an error within 2 per cent.

Experiment on the study of interferences : In a separate set of experiments, an aliquot of the standard solution containing 100 μg of chromium was taken in each of the several different separating funnels. To each of these, an aqueous solution of metal ions viz., Fe^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+} and the anions MoO_4^{2-}, WO_4^{2-}, MnO_4^-, CNS^-, $S_2O_3^{2-}$, F^-, $C_2O_4^{2-}$, VO_3^- and ClO_4^- in amounts equal to and three and five times the amount of chromium was added. The volume in each was made 5 ml by adding 1 *N* H_2SO_4. To each of these solutions was then added 1 ml of the tetraphenylarsonium chloride reagent. The resulting mixture was extracted as above with 5 ml of 1,2-dichloroethane and the absorbance of the organic phase was measured at 363 nm. Another aliquot containing 100 μg of chromium in absence of other ions was treated in a similar manner and the absorbance of the organic extract was measured at 363 nm.

Removal of interference due to

(a) *Oxalate :* An aliquot containing 100 μg of chromium was taken in two different separating funnels. To each of these solutions, a solution containing 100 μg and 500 μg of $C_2O_4^{2-}$ was added separately. The resulting solutions were warmed and a dilute solution of equivalent amount of $KMnO_4$ was added dropwise. The solutions were then treated with 2 ml of 10% ceric sulphate solution and were boiled for 10 min. The resulting solutions were made 1 *N* in H_2SO_4 and was extracted into *iso*butyl methyl ketone taking 5 ml of the solvent. Chromium in the organic phase was then back extracted to water and the aqueous layer was made 1 *N* with respect to H_2SO_4 to which 1 ml of tetraphenylarsonium chloride reagent was added. Extractions and absorbance measurements were made as described above. The amount of chromium calculated showed cent per cent recovery of chromium in both.

(*b*) *Permanganate* · An aliquot of the standard solution containing 100 μg of chromium was taken in two different separating funnels. To each of these, solutions containing 100 μg and 500 μg of MnO_4^- was added separately. Each of these solutions was warmed with 2 to 3 drops of absolute alcohol. The resulting colourless solutions were then treated with 2 ml of 10% ceric sulphate solution. Chromium as chromate was then separated, extracted and absorbance of the extract was measured in a similar manner as described above. A good recovery of chromium was obtained in both the cases.

Determination of chromium in high speed steel and alloy steel : 0.1 g of high speed steel (No. 64b) and 0.6 g of alloy steel (No. 60b), procured from the Bureau of Analysed Samples Ltd., was weighed out accurately in two different beakers. The alloys were then dissolved in the minimum volume of concentrated nitric acid by heating. To each of the solutions, after cooling, was added 2 ml of 50% H_2SO_4. The resulting mixture was heated till the evolution of white fumes. Solutions were then diluted and boiled with 2 ml of 10% ceric sulphate solution for about 10 min. Solutions were cooled and made 1 *N* in H_2SO_4 and were extracted with 10 ml of *iso*butyl methyl ketone for 3 min. Organic extracts were washed with 1 *N* H_2SO_4 and the dichromate was back extracted by shaking the organic layer repeatedly with distilled water. Combined aqueous layers were transfered into two separate 100 ml standard flasks and the required amount of 50% H_2SO_4 was added to make these 1 *N* in H_2SO_4 in the made up solution.

Separate aliquots from each solution were taken in different separating funnels, to each of which 1 ml of 0.01 *M* tetraphenylarsonium chloride reagent was added. Volume of the resulting solution was made 5 ml with 1 *N* H_2SO_4 and was then extracted with 5 ml of 1,2-dichloroethane. Absorbance in the organic layer was measured at 363 nm and the amount of chromium was calculated form the calibration curve. The average of a number of determinations from different weighed samples are shown below :

Samples	*Chromium found*	*Chromium present*
High speed steel (No.64b)	4.4%	4.55%
Alloy steel (No. 60b)	0.72%	0.75%

Discussion

Chromium(VI) forms ion pair with tetraphenylarsonium chloride and the resulting ion association compound, which is precipitated in aqueous solution, 1 *N* in sulphuric acid was found to be extractable into chloroform and 1,2-dichloroethane. Of the two solvents, 1,2-dichloroethane proved to be a better extractant for the ion pair which absorbed in the ultraviolet region having maximum absorption at 363 nm (Fig. 1). Beer's law is obeyed over the concentration range 10 to 40 μg of chromium per ml of the organic phase.

An examination of the interfering effect of a number of metal ions viz., Fe^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+} in varying amounts revealed that except Sb^{3+}, none of these ions interfered. The organic extract of Cr(VI)-TPA complex was found to be colourless in presence of Sb^{3+} probably due to the reduction of Cr(VI) by Sb^{3+}. Other metal ions did not interfere as there was no possibility of formation of their halo complexes capable of forming ion pair with tetraphenylarsonium chloride. Similar examination with anions, having possibility of ion pair formation with the reagent, viz., MoO_4^{2-}, WO_4^{2-}, MnO_4^-, $S_2O_3^{2-}$, CNS^-, F^-, $C_2O_4^{2-}$, VO_3^- and ClO_4^- were made. Of these

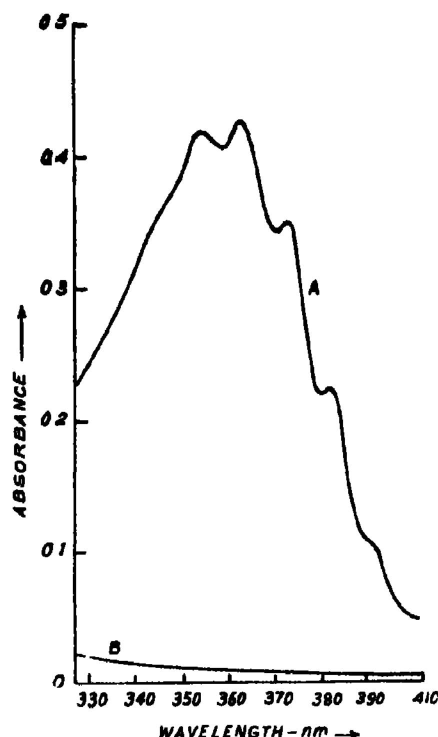


Fig. 1. Absorption spectra of (A) tetraphenylarsonium chromate in 1,2-dichloroethane containing 20 μg of chromium per ml against solvent (B) the reagent blank against solvent

only MnO_4^- and $S_2O_8^{2-}$ interfered even when present in amounts equal to chromium. Oxalate interfered only slightly. Thiocyanate, though did not interfere in equal amounts, interfered when present in five time excess. However, the relative ease of interconversion of Cr(III) to Cr(VI) made it possible to separate chromium from most of the commonly associated interfering elements.

Interference due to $C_2O_4^{2-}$ ion was removed by $KMnO_4$ oxidation. Chromium was then separated from any excess permanganate by extraction with *iso*butyl methyl ketone from 1 *N* sulphuric acid and it was determined subsequently by back extracting to water. Interference due to MnO_4^- ion was removed by reduction with alcohol when both MnO_4^- and CrO_4^{2-} were reduced. Chromium was later oxidised with ceric sulphate in acid solution, separated and estimated with good recovery of chromium.

The method was used for estimation of chromium in high speed steel and alloy steel and the amount of chromium found was in good agreement with the standard value with an error within 3 to 4 per cent.

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Extraction of Cerium(IV) by Liquid Cation Exchanger (Versatic 10) and its Separation from Lanthanide Elements

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A rapid and selective method for the extraction of cerium(IV) at milligram level with liquid cation exchanger, Versatic 10, in benzene was proposed. Quantitative extraction was achieved in the pH range 5.0-5.5. The effect of variables such as pH of the aqueous phase, diluent, contact time and extractant concentration on the extraction was studied. The equilibration between the two phases was achieved within one minute. The probable composition of the extracted species being CeR_4, was deduced from the extraction data. The presence of magnesium, calcium, cobalt, nickel, zinc, cadmium and mercury did not interfere in the extraction of cerium(IV). Cerium(IV) was quantitatively separated from several binary and ternary mixtures containing rare earth elements.

VERSATIC acids, viz., Versatic 911, Versatic 10 etc., have been shown to be promising extractants for large scale hydrometallurgical processing of divalent metals[1,2]. The composition of the extracted species of several metals using Versatic 911 and Versatic 10 were investigated by several workers[3-6]. These acids were extensively used in our laboratory for the extraction of di, tri and tetra valent metals[7-9]. However, no systematic attempt has yet been made to study the extraction behaviour of Ce(IV) with Versatic 10 and hence the title investigation. This offers a simple, rapid and selective method for the extraction and separation of cerium(IV) from lanthanide elements at milligram level. The proposed method is more selective than the methods reported earlier.

The extraction of metals by carboxylic acid takes place by a cation exchange mechanism. This can simply be expressed as



$$M^{n+} + n\,\overline{R-COOH} \rightleftharpoons \overline{M(R-COO)_n} + nH^+$$

Barred species are in the organic phase.

Experimental

Apparatus : Elico pH meter (ELICO, Model LI-10, Hyderabad, India) was used for the measurement of *p*H. Separatory funnels (250 ml) were used for extraction experiments.

Reagents Versatic 10 (purity, 99%) is a mixture of C_{10} isomeric tertiary monocarboxylic acid[10] It is manufactured and supplied by Shell Co. Ltd. (London) and was used without further purification.

Ceric sulphate solution (3.75 mg/ml) was prepared by dissolving about 3.0 g of $Ce(SO_4)_2$ $4H_2O$ (Chemapol, Czechoslovakia) in 200 ml of double deionised water to which 2 ml of concentrated H_2SO_4 (A. R.) was added. The solution was standardised by the complexometric titration with EDTA using xylenol orange indicator[11].

Ascorbic acid (B. D. H., A. R.) was used for the reduction of cerium(IV) during estimation. All other chemicals and solvents used were of analytical grade

Buffer solutions of different *p*H were prepared from 1 *M* sodium acetate solution and the *p*H were adjusted using chloroacetic acid (*p*H 1.5 to 2.5) and glacial acetic acid (*p*H 3.5 to 6).

General extraction procedure : The procedure of the experiment was based on solvent extraction technique. An aliquot (2 ml) of the test solution containing 7 5 mg of the metal ion was mixed in a 250 ml separatory funnel with 10 ml of buffer solution Sodium hydroxide solution was used for the adjustment of *p*H. The total volume of the aqueous phase was made 20 ml so that the ultimate concentration of cerium(IV) in the aqueous phase was 2.3×10^{-3} *M* The solution was equilibrated with 10 ml of 0.887 *M* Versatic 10 in benzene for 5 min. The equilibration time was varied from 0.5-10 min and it was found that distribution coefficient reached a constant value within 1 min. However, the equilibration time was fixed to 5 min. All the experiments were carried out at 30±1°. The phases, after equilibration, were allowed to settle for 10 min, the aqueous phase separated and equilibrium *p*H measured. The aqueous phase was washed with benzene (5 ml) to remove the entrained solvent and the amount of cerium(IV) present in that phase was estimated by complexometric titration The extracted cerium from the organic phase was stripped with 2 *N* nitric acid (20 ml) for 5 min and finally estimated by EDTA titration. Variations in procedure are indicated at appropriate places.

Results and Discussion

Effect of variables on the extraction :

*p*H : The extraction of cerium(IV) with Versatic 10 at various *p*H was performed using buffer solution of different *p*H. The results (Table 1) showed

that the extraction of cerium(IV) increases with increased pH of the aqueous phase and became quantitative at pH 5.0-5.5. It was observed that under ordinary experimental condition (in absence of acetate buffer) cerium(IV) starts hydrolysis at pH 4.0 which leads to difficulty in phase separation. This tendency was checked upto pH 5.5 by carrying out the extraction in presence of acetate buffer For all quantitative extraction the pH of aqueous phase was maintained at 5.0.

TABLE 1—EXTRACTION OF CERIUM(IV) AS A FUNCTION OF pH

pH	Extraction of cerium(IV), %	Distribution coefficient D
1.7	0.9	0.02
2.15	3.7	0.08
3.50	40.0	1.33
3.60	78.0	7.09
3.90	87.1	13.50
4.35	95.4	41.48
4.80	97.2	69.48
5.15	98.65	146.1
5.30	99.2	248.0
5.50	99.2	248.0

Various diluents : Cerium was extracted with Versatic 10 solution using various diluents (Table 2) The ratio of organic to aqueous phase was maintained at 1 : 2. Quantitative extraction of cerium(IV) was achieved in most of the cases. Benzene is the most suitable diluent and was used in all the experiments.

TABLE 2—EFFECT OF DILUENTS ON EXTRACTION OF CERIUM(IV)

Diluent	Dielectric constant	Ce(IV) Extracted, %
Carbon tetrachloride	2.21	97.25
Benzene	2.28	99.2
Xylene	2.36	99.2
Toluene	2.4	97.4
Diisopropyl ether	3.9	Emulsion formation
Chloroform	4.81	97.4
Butanol	16.1	97.25

Equilibration time : The contact time was varied from 30 sec to 10 min. The distribution coefficient reached a constant value within 1 min of shaking and back extraction was completed within 5 min Contact time and stripping time was kept 5 min in all the experiments. 2 N nitric acid (20 ml) was used for stripping cerium from the organic phase.

Versatic 10 concentration : The effect of extractant concentration on extraction was studied by varying the concentration of Versatic 10 from 3.4×10^{-2} M to 1.08×10^{-1} M using benzene as diluent. The extraction experiments were carried out at constant metal concentration (2.3×10^{-3} M) and constant pH. Plot of log D against log [Versatic 10] produced a straight line of slope = 1.9. Versatic 10 in benzene diluent exists as dimer[6], which indicates that four solvent molecules are entering into the extracted species. The probable extraction mechanism may therefore be represented as :



$$Ce^{4+}+2\,\overline{R_2H_2}\rightleftharpoons\overline{CeR_4}+4H^+$$

where R_2H_2 represents the dimeric form of Versatic 10 in benzene and barred species are in the organic phase.

Extractive separation : Cerium(IV) was separated from several binary mixtures using the recommended extraction procedure. The aqueous phase, containing 2.3×10^{-3} M of cerium(IV) and appropriate quantity of foreign ions, was equilibrated with 0.887 M Versatic 10 (10 ml) in benzene for 5 min at pH 5.0. The organic phase after equilibrium, was stripped with 2 N nitric acid (20 ml) for 5 min and cerium(IV) was estimated by complexometric titration. The amount of foreign ions coextracted with cerium were negligible in most of the cases. Calcium, magnesium, cobalt, nickel, zinc, cadmium and mercury did not interfere in the extraction. Cerium was separated from lanthanum, praseodymium, neodymium, samarium, godolium, dysprosium and terbium. The interfering ions are iron, copper, thorium and uranium. The effect of foreign ions and their tolerance limits are shown in Table 3.

TABLE 3—EFFECT OF FOREIGN IONS ON THE EXTRACTION OF CERIUM(IV) WITH VERSATIC 10 (pH 5.0)

Foreign ions	mg	Cerium Taken (mg)	Cerium Found (mg)	Error %
Mg^{2+}	10.0	7.5	7.44	0.84
Ca^{2+}	"	"	7.44	0.84
Co^{2+}	"	"	7.44	0.84
Ni^{2+}	"	"	7.5	0
Zn^{2+}	"	"	7.44	0.84
Cd^{2+}	"	"	7.44	0.84
La^{3+}	"	"	7.37	1.67
Pr^{3+}	"	"	7.44	0.84
Nd^{3+}	15.0	"	7.44	0.84
Sm^{3+}	8.0	"	7.37	1.67
Gd^{3+}	10.0	"	7.44	0.84
Dy^{3+}	5.0	"	7.37	1.67
Tb^{3+}	5.0	"	7.31	2.50
Hg^{2+}	10.0	"	7.46	0.56

Separation of cerium(IV) from synthetic mixtures : The recommended procedure for the extraction of Ce(IV) was applied to several synthetic mixtures produced by mixing 5 mg of each metal ion. The total volume of the aqueous phase was kept 20 ml and extracted with 0.887 M Versatic 10 (10 ml) in benzene. Extractions were carried out at pH 5.1 using suitable buffer solution. The results given in Table 4 show that in most of the cases quantitative recovery of Ce(IV) was achieved. The proposed method can therefore be applied for selective extraction and separation of Ce(IV) from rare earth mixtures present at milligram level. The method is simple and rapid in comparison to other methods reported earlier.

Table 4—Quantitative Recovery of Cerium(IV) from Rare Earth Mixtures Using Versatic 10 (pH 6.1)

Sample No	Synthetic mixture	Cerium(IV) Taken (mg)	Cerium(IV) Found (mg)	Error %
1.	Ce(IV) + La(III) + Pr(III)	7.5	7.5	0
2.	Ce(IV) + Pr(III) + Nd(III)	,,	7.5	0
3.	Ce(IV) + Nd(III) + Sm(III)	,,	7.48	0.2
4.	Ce(IV) + Sm(III) + Gd(III)	,,	7.42	1.0
5.	Ce(IV) + Gd(III) + Tb(III)	,,	7.44	0.84
6.	Ce(IV) + Tb(III) + Dy(III)	,,	7.41	0.81
7.	Ce(IV) + La(III) + Pr(III) + Nd(III)	,,	7.42	1.0

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Titrimetric Determination of Thorium(IV) using N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid as Titrant and Pyrocatechol Violet as an Indicator

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Thorium(IV) has been determined by visual titration with N-(2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) around pH 2.5, using pyrocatechol violet (PCV) as an indicator at room temperature. The colour change is from pink to lemon-yellow. The optimum range for the estimation was found to be 6.0 μg to 1.19 mg Th per ml in a total volume of 75 ml. The relative standard deviation for 16 samples in 2 different concentrations (i.e. 6.3 μg/ml to 63 μg/ml Th in the optimum range) was found to be in the range of 1.3% to 0.45%. The optimum conditions like pH, concentration of HEDTA, concentration of indicator, temperature were also established and described. The interference of foreign ions was also studied and their tolerance limits were established and described.

TITRIMETRIC methods for the determination of thorium are not many. In the earlier methods disodium salt of EDTA was used as titrant[1,2]. Apart from EDTA, nitrilotriacetic acid (NTA)[3] and disodium salt of anthranilic-N,N-diacetic acid (ANDA)[4], *trans*-1,2 diaminocyclohexanetetraacetic acid (DCTA)[5] and triethylenetetraminehexaacetic acid (TTHA)[6] were also introduced for the titration of thorium with some indicators. In our comparative study of various titrants for the titrimetric determination of thorium using various indicators and titrants, we studied HEDTA as a titrant and pyrocatechol violet as an indicator.

Experimental

Thorium(IV) solution : A 0.1 *M* solution of thorium nitrate [$Th(NO_3)_4.6H_2O$] (Fischer Scientific Co., USA) was prepared with a few drops of nitric acid to prevent the hydrolysis of thorium and was standardized gravimetrically by the conventional benzoic acid method[7].

HEDTA solution : A 0.1 *M* solution of HEDTA (Aldrich Chemical Company, Inc., USA) was prepared in distilled water with a few drops of sodium hydroxide to give a clear solution.

Pyrocatechol violet (PCV) (GR) : A 0.1% aqueous solution of PCV (Loba. Chemie. Industranal Co., Bombay) was prepared.

All other solutions were prepared from A. R. quality reagents in distilled water.

Procedure : The solution of thorium(IV) is diluted until it contains 0.4468-89.36 mg of the metal per 75 ml of solution (i.e. 0.0059 mg/ml – 1.19 mg/ml). The *p*H is adjusted to 2.3-3.0 and 3 drops of the PCV solution is added. This is titrated with 0.01 *M* solution of HEDTA until the colour changes from pink to lemon-yellow.

One ml of 0.01 *M* HEDTA is equal to 2.321 mg of Th.

Results and Discussion

pH variation : Two ml of 0.1 *M* solution of thorium(IV) was taken and diluted to 75 ml, *p*H adjusted to different value between 1.0 and 3.5, and it was found that the end point was sharp between 2.3 to 3.0. Below this *p*H range the end point was not observed at all and above this *p*H range the precipitation of thorium(IV) was observed. Between *p*H 2.3 and 3.0, the results were accurate and reproducible. In all further experiments *p*H was maintained at 2.5 ± 0.1

HEDTA variation : HEDTA concentration was varied from 0.001*M* to 0.1 *M* while titrating 2.0 ml of thorium(IV) (4.46 mg Th in 75 ml) (i.e. 0.059 mg/ml) at *p*H 2.5. It was observed that 0.01*M* HEDTA is the best concentration of the titrant that can be used. In other cases the error was slightly more. So in all further studies the titration was performed with 0.01 *M* HEDTA only.

Indicator variation : Indicator was varied from 1 to 10 drops of 0.1% solution and it was found that in all cases the end point was sharp. 3 drops of indicator is sufficient to judge the end point with the naked eye easily. Hence in further titrations only 3 drops of indicator (0.1% solution) was added.

Temperature study : The end point as described above was sharp even at room temperature throughout the thorium(IV) concentration range estimated. Above and below the range mentioned, the end point was not sharp. At much higher concentrations of thorium(IV) the titration could be

carried out if the temperature near the end point is maintained at 50°. But it was felt unnecessary to go for higher concentrations of thorium(IV) as at room temperature the end point was sharp with lower concentrations of thorium.

Range, relative standard deviation: According to the procedure described above the optimum concentration of thorium(IV) that can be titrated was found to be 0.0159 mg/ml-1.19 mg/ml (in a total volume of 75 ml). Below and above this range the end point was not sharp. Relative standard deviation of 16 samples in 2 different concentrations of thorium in the optimum range was found to be in the range of 1.3% to 0.45%.

Effect of foreign ions: The following foreign ions do not show any significant error in the estimation of 1.16 mg of thorium in 75 ml according to the procedure described above.

K(I) 2000.0 mg (1818 times); Ba(II) 2000.0 mg (1818 times); Mn(II) 1000.0 mg (909 times); Sr(II) 1000.0 mg (909 times); Mg(II) 500.0 mg (454.5 times); Ca(II) 480.0 mg (436.3 times), U(VI) 150.0 mg (136.3 times); Cr(III) 60.0 mg (54.5 times); Cd(II) 40.0 mg (36.3 times); Pb(II) 26.0 mg (23.6 times); rare earths(III) 25.0 mg (22.7 times); Al(III) 20.0 mg (18.0 times); Cu(II) 5.0 mg (4.5 times). However Zr(IV), Fe(III), Sn(II) and Ti(IV) cause serious interference even if present at 1.0 mg level and should be eliminated before titration.

Among the anions fluoride, sulphate, phosphate and oxalate cause serious interferences. Nitrate and chloride do not interfere at all.

Thorium(IV) forms a pink coloured complex with PCV at *p*H 2.0-3.0 and by treatment with HEDTA this pink colour is changed to lemon-yellow around *p*H 2.5. This reaction has been utilized for the titrimetric determination of thorium using PCV as indicator. Since the titration is carried out in an acidic solution comparatively few cations form complexes with HEDTA of sufficient strength to interfere. Thorium can be estimated in presence of the above mentioned foreign ions.

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Extraction and Photometric Method for the Simultaneous Determination of Palladium(II) and Platinum(IV) with Dibenzylidenethiocarbohydrazide

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Dibenzylidenethiocarbohydrazide (DBTCH) reacts with palladium(II) at room temperature in the pH range of 5.0-7.5 and with platinum(IV) under hot condition in the pH range of 5.8-6.8. The complexes are yellow in colour and are quantitatively extracted in ethyl acetate and chloroform respectively and exhibit maximum absorption at 370 nm. Both the metals form 1 : 2 complex (metal to ligand) with the ligand. The compositions of the complexes are established by mole-ratio and slope-ratio methods. The stepwise and overall formation constants of the complexes are determined by extended Yatsimirskh's, Leden's and Harvey-Manning's methods. It has been shown that DBTCH may be employed for simultaneous determination of palladium(II) and platinum(IV) by extractive spectrophotometric method. The effect of the other commonly associated ions in the determination of palladium and platinum have also been studied.

BEAMISH[1] reviewed the colorimetric methods for the determination of palladium(II) and platinum(IV) and only a few reagents had been recommended for the simultaneous determination of palladium and, platinum. Recently α-benzoin oxime[2] was used as a chelating agent for the spectrophotometric determination of palladium(II) and platinum(IV) in presence of each other. But the sensitivities of the reagent for the determination of palladium and platinum were low. Moreover, a number of commonly associated base metals and other platinum metals interfered with the determination. Mizuno and Miyatani[3] recommended 4-(2-pyridylazo) resorcinol for successive spectrophotometric determination of palladium(II) and platinum(IV). The sensitivity of the reagent was high for the determination of palladium but the presence of palladium gave a positive error in the determination of platinum and vice versa. 1,4-Diphenylthiosemicarbazide[4] was also employed as a complexing agent for the simultaneous spectrophotometric determination of palladium(II) and platinum(IV).

Dibenzylidenethiocarbohydrazide (DBTCH), which was used as a sensitive and selective reagent for the spectrophotometric determination of ruthenium(III)[5], has been utilised as a very sensitive reagent for the extractive spectrophotometric determination of palladium(II) and platinum(IV). A method has been described for their simultaneous determination. The method is based on the fact that palladium(II) forms complex with DBTCH at room temperature and platinum(IV) forms complex with the reagent only on heating. The platinum content in the mixture should not exceed ten times by weight of palladium.

Experimental

Apparatus and reagents : A Carl-Zeiss VSU spectrophotometer with 1.0 cm matched silica cells was used for absorbance measurements. The *p*H values of the solutions were measured with an expanded scale *p*H meter of Systronic.

The stock solutions of palladium(II) and platinum(IV) were prepared by dissolving 1.0 g each of palladium(II) chloride (J. M.) and chloroplatinic acid. The palladium(II) solution was standardised gravimetrically using dimethylglyoxime[6] and platinum(IV) solution by thiosalicylamide[7] as chelating agents. Solutions for the spectrophotometric determinations were prepared by dilution of the stock solution with distilled water.

The reagent was insoluble in water and only moderately soluble in ethanol. A 1.4×10^{-3} *M* reagent solution was prepared in ethanol. All other chemicals and reagents were of analytical grade.

Buffer solution : 10% sodium acetate and 3 *M* hydrochloric acid solutions were used to adjust the solutions at different *p*H values.

Procedure

Spectrophotometric determination of palladium(II) : A known amount of palladium(II) solution (6.0-65 μg of metal) was taken in a 100 ml separatory funnel, diluted to 20 ml with distilled water and the *p*H of the solution was adjusted to 5.0-7.5. 2-3 ml ethanol and 2 ml reagent solution ($[R]/[M] \geq 5.0$) were added. The mixture was thoroughly mixed and allowed to stand for 2 hr, extracted thrice with 5 ml portions of ethylacetate

and washings collected in a 25 ml volumetric flask. It was made upto volume with ethylacetate, dried and absorbance was measured at 370 nm against the reagent blank.

Spectrophotometric determination of platinum(IV) : An aliquot containing 10-175 μg of platinum(IV) was taken in a 100 ml separatory funnel, diluted to 20 ml with distilled water and *p*H of the solution was adjusted to 5.8-6.8 2-3 ml ethanol and 2 ml reagent solution ([R]/[M]$\geq$5.0) were added and heated over boiling water bath for 30 min. It was then cooled to room temperature and extracted thrice with 5 ml portions of chloroform and collected in a 25 ml volumetric flask. It was then diluted to the mark, dried and absorbance was measured at 370 nm against the reagent blank

Simultaneous spectrophotometric determination of palladium(II) and platinum(IV) in a mixture : An aliquot containing known amount of palladium and platinum was taken in a 100 ml separatory funnel, diluted to 20 ml with distilled water and the *p*H of the solution was adjusted to 5.8-6.8. The palladium in the mixture was extracted and estimated according to the procedure described above. After the separation of palladium from the mixture, the platinum content in the residual aqueous phase was estimated according to the procedure described earlier.

Results and Discussion

Absorbance curves : The absorbance curves of the extracts of palladium(II)-DBTCH complex in ethylacetate and platinum(IV)-DBTCH complex in chloroform and the absorbance curves of the reagent blanks are shown in Fig 1 and Fig. 2 respectively Both the complexes showed maximum

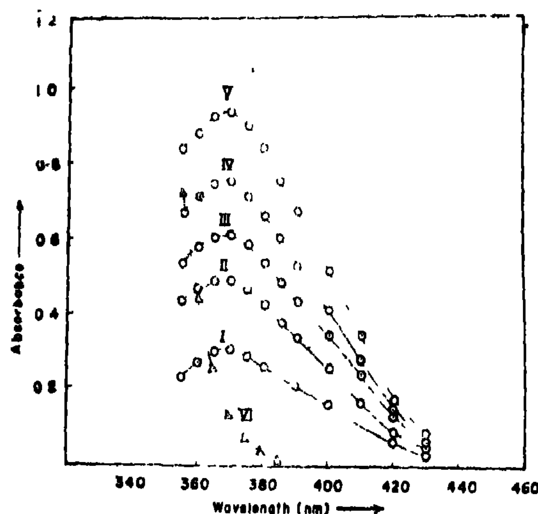


Fig 1. Absorbance curves of Pd(II)-DBTCH complex and reagent blank in ethylacetate.

[Pd^{+2}] : (I) $0.72\times10^{-5}M$, (II) $1.08\times10^{-5}M$, (III) $1.44\times10^{-5}M$, (IV) $1.80\times10^{-5}M$, (V) $2.16\times10^{-5}M$; [DBTCH] : (VI) $1.08\times10^{-5}M$.

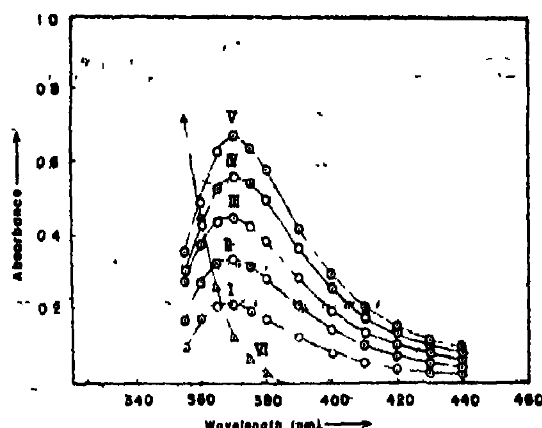


Fig 2. Absorbance curves of Pt(IV)-DBTCH complex and reagent blank in chloroform.

[Pt^{+4}] : (I) $0.749\times10^{-5}M$, (II) $1.124\times10^{-5}M$, (III) $1.498\times10^{-5}M$, (IV) $1.878\times10^{-5}M$, (V) $2.248\times10^{-5}M$, [DBTCH] : (VI) $1.124\times10^{-5}M$.

absorbance at 370 nm. The absorbance values of the reagent blanks were appreciably low in this region

The effect of acidity, temperature, concentration of the reagent and the stability of the complexes : The study of the extraction behaviour of the complexes showed that quantitative extraction of palladium(II)-DBTCH complex occurred at *p*H 5.0-7.5 and platinum complex at *p*H 5.8-6.8.

Palladium formed a yellow coloured complex with DBTCH instantaneously at room temperature. The reaction was slow. The reaction mixture should be allowed to stand for at least 1.5 hr to attain maximum complex formation. The complex decomposed at higher temperature. Platinum did not form any complex with DBTCH at room temperature even on prolonged standing and at least 30 min of heating over boiling water bath was necessary for complete formation of the complex.

For maximal development of colour and for complete extraction of both the complexes the molar ratio of reagent to metal should exceed 5 : 1. Both the complexes were stable and the colour intensities of the complexes were constant over the studied 24 hr period.

Effect of solvents : Ethylacetate and chloroform were taken as working solvents for the extraction of palladium and platinum complexes respectively. Behaviour of a few other solvents along with ethylacetate and chloroform towards extraction of the complexes are shown in Table 1.

Calibration curve, optimum range and photometric error . Both palladium(II)- and platinum(IV)-DBTCH complexes obeyed the Beer's law at 370 nm over the concentration ranges of 0.2-3.0 ppm of palladium(II) and 0.5-7.0 ppm of platinum(IV) respectively.

TABLE 1—EXTRACTIONS OF THE PALLADIUM(II)- AND PLATINUM(IV) DBTCH COMPLEXES IN DIFFERENT SOLVENTS

Solvent	Pd(II) DBTCH complex		Pt(IV)-DBTCH complex	
	Distribution ratio	% Extracted	Distribution ratio	% Extracted
Benzene	2.678	72.04	4.58	81.98
Chloroform	24.01	96.01	181.7	99.5
1,2-Dichloroethane	7.5	88.2	35.52	97.25
Ethylacetate	71.0	98.6	548	99.8
Isobutyl methyl ketone	6.075	85.9	2.45	71.0

TABLE 2—CHARACTERISTICS OF THE ANALYTICAL METHODS FOR THE DETERMINATION OF PALLADIUM AND PLATINUM WITH DBTCH

Type of the complex	Molar absorptivity $l\ mol^{-1} cm^{-1}$	Sandell's sensitivity $\mu g\ cm^{-2}$	Relative mean error %	Standard deviation	Coefficient of variation %
Pd(II)-DBTCH	4.268×10^4	0.0025	1.04	0.32	1.12
Pt(IV)-DBTCH	2.9768×10^4	0.0065	0.55	0.28	0.51

TABLE 3—STEPWISE AND OVERALL STABILITY CONSTANTS FOR PALLADIUM(II) AND PLATINUM(IV) COMPLEXES AT 27±2°

Method	Palladium(II)-DBTCH			Platinum(IV)-DBTCH		
	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$
Yatsimirskii's	5.6108	5.3280	10.9388	5.8771	5.4860	11.3631
Leden's	5.6232	5.3310	10.9542	5.8062	5.3177	11.1239
Harvey-Manning's	5.7057	5.7057	11.4115	5.7759	5.7759	11.5518

The optimum concentration ranges with the highest accuracy as evaluated from Ringbom's[8] curve were 0.6-2.0 ppm for palladium(II) complex and 1.6-5.0 ppm for platinum(IV) complex. The corresponding values of relative analysis error per one percent photometric error according to Ayre's[9] equation were 2.73% for the determination of 1.0 ppm palladium and 2.72% for the determination of 3.0 ppm platinum.

Characteristics of the analytical methods : Molar absorptivity of the complex and the sensitivity[10] of the colour reaction are shown in Table 2. The relative mean errors and the relative standard deviations obtained from five identical sets of experiments are also given.

Five determinations with 28.8 μg of palladium gave an average of 28.53 μg which varied between 28.53±0.30 μg at 90% confidence limit.

With 54.8 μg platinum the average values was 54.5 μg which varied between 54.5±0.27 μg at 90% confidence limit.

Nature and composition of the complexes and their successive formation constants : The composition of the palladium(II)- and platinum(IV)-DBTCH complexes were studied by mole-ratio[11] method and verified by slope-ratio[12] method. It was found that in both cases a 1 : 2 (metal : ligand) complex was formed.

The conditional stepwise stability constants of the complexes were computed from spectrophotometric data of Yatsimirskii's[13,14] and Leden's[15] method. The results of all the systems along with the values of overall stability constants by Harvey-Manning's method are compiled in Table 3.

TABLE 4—EFFECT OF DIVERSE IONS ON THE DETERMINATION OF PALLADIUM(II) AND PLATINUM(IV)

Foreign ion added	Amount (in mg) tolerated in the determination of Palladium(II) (Pd = 28.8 μg)	Platinum(IV) (Pt = 54.8 μg)
Ti(IV)	1.0^b	1.0^b
V(V)	2.5	1.0
Cr(III)	1.0^b	1.0^b
Mn(II)	1.0^b	1.0^b
Fe(III)	1.0^b	1.0^b
Co(II)	1.0^a	1.0^a
Ni(II)	1.0^a	1.0^a
Cu(II)	0.15^d	0.10^d
Zn(II)	2.5^a	1.0^a
Cd(II)	2.5^a	1.0^a
Hg(II)	0.5^c	0.5^c
Pb(II)	$1.0^{a,b}$	$1.0^{a,b}$
Mo(VI)	1.5	1.0
W(VI)	1.5	1.0
U(VI)	1.5	1.0
Os(VI)	1.0^e	nil
Pd(II)	—	nil
Pt(IV)	0.30	—
Ru(III)	0.20^f	0.05^f
Rh(III)	nil	nil
Ir(III)	0.50	nil
Citrate	200	100
Oxalate	200	100
Tartarate	1000	500
Phosphate	200	200
EDTA	50	50
Fluoride	500	500
Iodide	2000	2000

a = in presence of Ca-EDTA, b = in presence of tartarate, c = in presence of iodide ; d = in presence of Na_2-EDTA, e = prior reduction with SO_2, f = in presence of citrate.

Effect of diverse ions : In the study of the effect of diverse ions, the standard palladium(II) and platinum(IV) solutions containing known amounts of metals were mixed with varying amounts of diverse ions and the recommended procedures were followed. The tolerance limits (i.e. concentrations of the diverse ions causing an error of less than ±2% in the transmittance value) are recorded in Table 4.

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The authors are grateful to U. G. C., Govt. of India for the award of a Teacher Fellowship to one of them (J. P.). The authors also record their sincere thanks to Dr. S. C. Shome, U.G.C., Retired Professor of Chemistry for valuable suggestions and encouragement.

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Extraction and Spectrophotometric Determination of Silver(I) with 4-S-Benzyl-1-p-Chlorophenyl-5-Phenyl-2, 4-Isodithiobiuret (BPPTB)

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4-S-Benzyl-1-*para*chlorophenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) was used for the quantitative extraction of silver at trace level. Silver was extracted quantitatively at *p*H 6.1-7.7 with 0.002 *M* BPPTB in chloroform. The solution exhibits peak of maximum absorption at 500 nm. The system followed Beer's law in the concentration range of 1.1 to 21.5 μg/ml of silver. The complex was stable for 2 hr. 10 ml of 0.002 *M* BPPTB in chloroform was sufficient for quantitative extraction of silver. The optimum period of agitation was 5 min. It was possible to achieve extractive separation and colorimetric determination of silver in the presence of a large number of cations and anions.

4-S-BENZYL-1-*para*chlorophenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) has been used for extraction of Pd(II), Pt(II), Rh(III) and Cu(II)[1-4]. These elements have been separated and estimated using spectrophotometric technique. The simultaneous spectrophotometric determination of these metals using BPPTB have also been reported[5]. The solid complexes of some transition metal complexes have been isolated and studied[6]. In the present paper the use of BPPTB for extractive separation of silver from various cations has been discussed.

Several chelating agents have been reported for the extraction of silver but only dithiozone, oxine, cupral and diluted tributyl phosphate were found to be effective for its separation at microgram levels[7,8]. The ion-association complex of silver with salicylic acid and dibutylamine has been extracted with isobutyl methylketone[9] but the ternary complex with *o*-phenanthroline-bromopyrogallol red[10] proved to be the most useful for selective extraction. *Bis* (2-ethylhexyl)phosphoric acid (HDEHP)[11] and diethyldithiophosphoric acid[12] have also been used as extractants, but only inefficiently, for the extraction of silver. Silver has also been extracted by thiodibenzoylmethane[13].

The proposed method is simple, rapid and affords clear-cut separation of silver at trace level from large number of ions.

Experimental

Apparatus and reagents : Beckman model DU-2 spectrophotometer with 10 mm light path quartz cells, ELICO *p*H-meter model LI-LOT, to and fro action flask shaker were used in this study.

4-S-Benzyl-1-*para*chlorophenyl-5-phenyl-2,4-isodithiobiuret (BPPTB) was synthesized as reported earlier[1]. About 0.002 *M* BPPTB in chloroform was used. The fresh solution of reagent was used.

About 0.001 *M* solution of silver nitrate (AnalaR, B. D. H.) was used and standardized volumetrically[14]. The dilute solution containing 54 μg/ml of silver was prepared from stock solution by suitable dilution. The solution was stored in dark and standardized regularly.

General procedure : An aliquot of the solution containing 54 μg of silver was taken. After addition of 10-15 ml of water the *p*H of the solution was adjusted to 6.1-7.7 on a *p*H-meter using sodium acetate (0.1 *M*) and acetic acid (0.1 *M*). The volume of the aqueous phase was made upto 25 ml. The solution was then transferred to a separating funnel after addition of 10 ml 0.002 *M* BPPTB in chloroform and shaken on a flask shaker for about 5 min. The layers were allowed to separate, the separation being enhanced with the addition of borax buffer of *p*H 12.0. The aqueous phase was removed and the organic phase was measured at 500 nm against a reagent blank prepared similarly. The amount of silver extracted was computed from the calibration curve.

Results and Discussion

Absorption spectra : The absorption spectra of silver-BPPTB complex ($Ag = 5.0\times10^{-5}$ *M*) against the reagent blank was taken. It is observed that the complex exhibits maximum absorbance at 500 nm. Hence all absorption measurements were taken at 500 nm. The molar absorptivity at 500 nm is 1.12×10^{4}. The Sandell's sensitivity[15] is 0.0096 $\mu g/cm^2$ at 500 nm.

Extraction as a function of pH *:* The extraction of silver was carried out at *p*H from 3-12 with BPPTB-chloroform. The results show that the extraction commenced at about *p*H 5.0 and was quantitative in the *p*H region of 6.1-7.7. The extraction was incomplete below and above these *p*H. Thus, the optimum *p*H for extraction is 6.1-7.7.

Beer's law : Different amounts of silver, ranging from 11 to 215 μg of silver per 10 ml of solution, were taken. They were extracted at pH 6.3 with 10 ml of 0.002 M BPPTB in chloroform. The absorbance of the complex was measured at 500 nm against the reagent as a blank. It was noted that the system adhered to Beer's law in the concentration limit of 1.1 to 21.5 μg of silver per ml at 500 nm.

Effect of BPPTB concentration : The silver was extracted at pH 6.3 with varying volumes and varying concentrations of the reagent. The results show that 10 ml of 0.002 M BPPTB was sufficient for quantitative extraction of silver. The extraction was incomplete at lower concentration of reagent. At higher concentrations of the reagent there was no increase in the absorption Thus, the optimum reagent concentration is 0.002 M.

Stability of the colour of the complex : The absorption of the colour of the complex was measured at elapsed intervals of 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 8.0 hr. It was observed that the complex was stable only for 2 hr. Light affects the stability of colour. The extract stored in dark is stable for 4 hr

Period of agitation : Varying the equilibration period from 1.0 to 15 min revealed that extraction is quantitative within 2 min of agitation. The extraction time of 5 min was arbitrarily chosen for further studies.

Effect of foreign ions : The effect of several ions on the extraction behaviour of silver was studied The tolerance was set at an amount needed to cause ±2% error in the recovery of silver. The results show that hundred times excess of Pb(II), Tl(III), Bi(III), Sb(III), As(III), Fe(III), phosphate, ascorbate and $EDTA^{4-}$, twenty times excess of Ru(III), Rh(III), Pt(IV), Ir(III), Th(IV), Ce(IV) and ten times excess of Au(III) and fluoride did not interfere in the extraction and determination of 54 μg silver at pH 6.3 with 10 ml 0.002 M BPPTB in chloroform. It was also observed that silver could be separated from the five times excess Re(VI), two times excess molybdate and equal amount of Hg(II), Zn(II) and Mn(II) by this method. Pd(II) and Ni(II) in half excess could be tolerated whereas Cu(II) and Co(II) interfered seriously.

Effect of solvents : Various solvents were tried to study the effect of solvents on extraction of silver with BPPTB. It was observed that clear-cut separation and quantitative extraction took place with chloroform and benzene.

The absorbance of the solution for 54 μg silver from 15 determinations is found to be 0.560±0.010. The relative standard deviation is ±1.2%. The method is applicable at trace concentrations of silver. It is possible to accomplish clear-cut separation of silver from various ions such as gold, lead, rhodium, ruthenium, platinum, iridium, lead, mercury and zinc with which it is usually associated. The method is rapid as the total time of separation is less than 30 min.

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Vulcanization of Natural Rubber : Influence of Hydrofuramide on Sulphenamide Acceleration System

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Influence of hydrofuramide (a reaction product of furfural and ammonia) on cure characteristics of sulphenamide accelerated sulphur vulcanization of natural rubber is reported. Presence of hydrofuramide causes a significant reduction in induction time, scorch time and optimum cure time though the overall cure rate and crosslink density do not increase. The effect of hydrofuramide on apparent energy of activation of vulcanization is negligible. The physical properties of the vulcanizate are also not affected by the presence of hydrofuramide. The sharp reduction in induction time in presence of hydrofuramide is attributed to reductive fission of sulphenamide by hydrogen sulphide (produced by the reaction of elemental sulphur with hydrofuramide).

INFLUENCE of hydrofuramide on thiuram vulcanization[1-4] and on thiazole[4] acceleration system was reported earlier. The work is now extended to sulphenamide acceleration system

Experimental

Method of preparation and analytical data of hydrofuramide, quality of natural rubber (NR) and other ingredients used in this work are the same as described earlier[1,2,3]. The sulphenamide used in this study was CBS, (N-cyclohexyl benzthiazyl 2-sulphenamide).

Mixing and vulcanization : Mixing and vulcanization procedure has been described earlier[1,2,4]. The vulcanization temperature in this work was 150°.

Rheometric study and energy of activation : Cure characteristics of the compounds were studied using Monsanto Rheometer (R100). The various cure parameters calculated from rheograph, e.g., t_{90}, t_{max} etc. have been defined earlier[1,3]. The apparent energy of activation was calculated from the slope of the straight line plots of log t_{60} against reciprocal of absolute temperature[6,7].

Determination of free sulphur and combined sulphur : Free sulphur in the vulcanizate was determined by sodium sulphite method following the standard ASTM procedure[8]. Combined sulphur was determined from the acetone extracted vulcanizate[1] by zinc nitric acid process in accordance with the standard ASTM procedure[8].

Determination of crosslink density and crosslink efficiency : Physical crosslink density of the vulcanizate was determined by equilibrium swelling method using Flory Rehner's[9] equation as described earlier[1,2,7]

Chemical crosslink density was computed using Mullins[10] equation from physical crosslink density and elastic constant as described earlier[4,7]. Crosslink efficiency was determined by dividing combined sulphur with chemical crosslink density[7]

Results and Discussion

Rheometric study and energy of activation : The cure characteristics of gum vulcanizates containing varying levels of hydrofuramide are shown in Fig. 1, while the cure characteristics of HAF (N-330) black filled compound containing varying levels of hydrofuramide is shown in Fig. 2. The various parameters calculated from the rheographs are given in Table 1.

It can be observed from Fig. 1 and Table 1 that the incorporation of hydrofuramide slightly reduces the minimum viscosity of the compound. There is a significant reduction in induction time as well as scorch time with increasing level of hydrofuramide. Induction time is 6.8 min for the control compound (containing no hydrofuramide) while that for the compound containing 3 phr hydrofuramide is 1.84 min. There is also a reduction in optimum cure time with increasing levels of hydrofuramide.

However, it is interesting to note that although hydrofuramide causes a reduction in scorch and induction time, as well as in optimum cure time, the ultimate torque as well as cure rate is not increased by the presence of hydrofuramide.

* All communication to be done at this address.

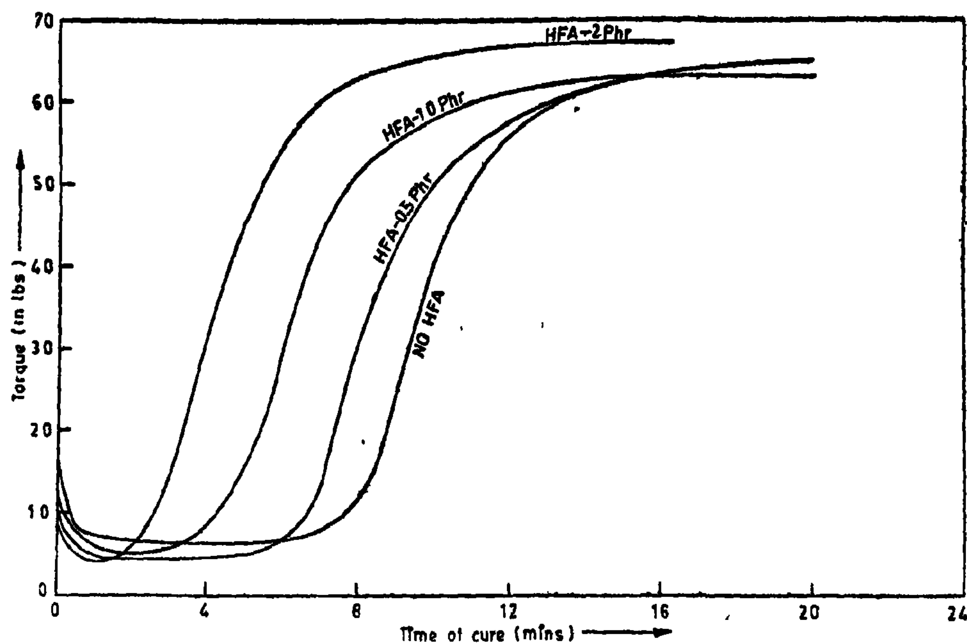


Fig. 1. Effect of hydrofuramide on cure characteristics of sulphenamide accelerated sulphur vulcanization system. Base formula : NR-100, ZnO-5, St acid-2, CBS-0.8, S-2.5 hydrofuramide (HFA)-variable. Rheograph ; Temp. 150°, Arc-3°.

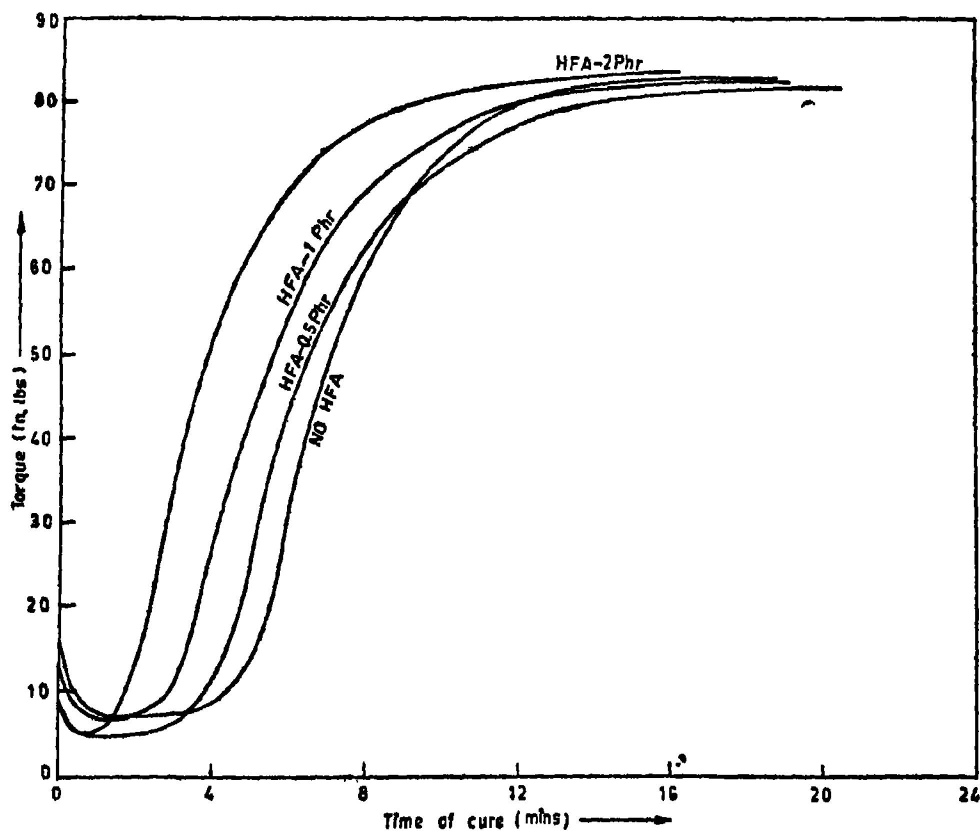


Fig. 2. Effect of hydrofuramide on cure characteristics of sulphenamide accelerated sulphur vulcanization system. Base formula : NR-100, HAF-50, ZnO 5, St. acid-2, CBS-0.8, S-2.5, hydrofuramide (HFA) variable. Rheograph : Temp 150°, Arc-3°.

TABLE 1—PARAMETERS CALCULATED FROM RHEOGRAPHS (Fig. 1 and Fig. 2)

	Fig. 1				Fig. 2			
Rheograph	1	2	3	4	1	2	3	4
Hydrofuramide (phr)	2	1	0.5	–	2	1	0 5	–
Minimum viscosity	3.7	4.2	4.7	6 2	4.6	4.7	5	6.7
Induction time (t_i) min.	1.81	2.90	5.20	6.80	1.25	2 0	2.70	3.70
Scorch time (t_s) min.	1.94	3.10	5.55	7.20	1 85	2 85	3.20	4.05
Opt. cure time (t_{90}) min	7.15	9.55	11.85	12.95	7.45	9 55	10 83	11.05
Max. cure (t_{max})	66.7	63.1	63.0	64 4	65 1	62 2	62.1	58 6
Cure rate index	19.19	15.50	15.87	17.39	16.39	13.89	13.16	14.29

The cure characteristics of the (N-330) black filled compound containing varying levels of hydrofuramide (Fig. 2) also follow the same trend as the gum compound – that is, incorporation of hydrofuramide reduces the induction time, scorch time and optimum cure time. There is no significant improvement in cure rate as well as t_{max} with incorporation of hydrofuramide. The Arrhenius plots of gum compounds containing varying levels of hydrofuramide is shown in Fig. 3. The plots of log t_{90} against reciprocal of absolute temperature follow a straight line pattern suggesting that Arrhenius equation holds good in the range studied. The apparent energy of activation, E (calculated from the slopes of the above straight line plots), is indicated on the graphs. It is apparent from Fig. 3 that incorporation of hydrofuramide causes no reduction in E value. All the four plots (control compound and three compounds containing 0.5 phr, 1 phr and 2 phr of hydrofuramide) are almost parallel. This suggests that hydrofuramide, although it shortens induction time and scorch time, does not activate (or promote) the overall vulcanization reaction of natural rubber accelerated by sulphenamide.

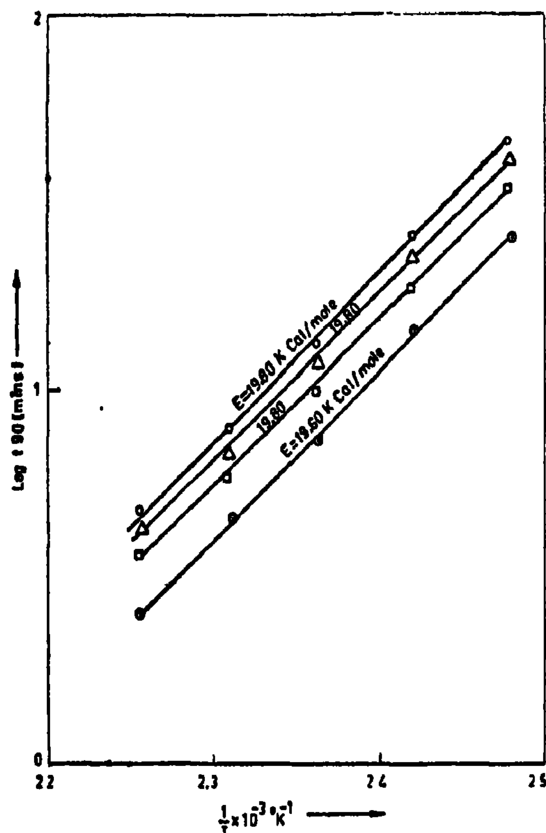


Fig 3. Effect of hydrofuramide on energy of activation in sulphenamide accelerated sulphur vulcanisation system.

Base formula : NR-100, ZnO-5, St. acid-2, CBS-0.8, S-2.5. Arrhenius plots :
○—No hydrofuramide △—0 5 phr hydrofuramide
□—1 phr hydrofuramide ○—2 phr hydrofuramide

The apparent energy of activation of N-330 (HAF) filled compound containing varying level of hydrofuramide is given in Table 2.

TABLE—2

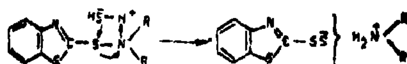
Compound	E Kcal/mole
Control (No hydrofuramide)	18.57
Compound containing 0.5 phr hydrofuramide	18.75
Compound containing 1 phr hydrofuramide	18.75
Compound containing 2 phr hydrofuramide	18 88

Thus in the case of black filled compounds also, incorporation of hydrofuramide causes no reduction in apparent energy of activation. The sharp decrease in induction period as well as scorch time due to the incorporation of hydrofuramide can be explained as follows. In sulphenamide system the period of induction and scorch time depends on the amine group attached to the thiazole to give the corresponding sulphenamide accelerator. In the sulphenamide acceleration system the actual accelerator precursor is the amine salt of MBT.

As suggested by Scheele and coworkers[11] the amine salt of MBT is the first product of sulphenamide formed which then reacts rapidly with the zinc oxide or zinc soap to give an amine addition complex which is the active accelerator leading to activation of elemental sulphur.

The ease of formation of amine salt of MBT from the sulphenamide would decide the length of induction period in sulphenamide accelerated vulcanization system. Since incorporation of hydrofuramide causes a significant reduction in induction

time and scorch time, hydrofuramide evidently promotes the decomposition of sulphenamide. The mode of action of hydrofuramide to facilitate the decomposition of sulphenamide could probably be due to reductive fission of S – S and/or S – N bonds by hydrogen sulphide with elemental sulphur as shown below :



Formation of H_2S by interaction of sulphur with hydrofuramide has been reported earlier[8].

The incorporation of hydrofuramide, though promotes the decomposition of sulphenamide (as shown above), does not increase the cure rate significantly, neither there is a reduction in apparent energy of activation. This suggests that it does not promote the rate determining step of sulphenamide accelerated sulphur vulcanization of natural rubber.

Thus hydrofuramide, being a weaker base compared to cyclohexylamine (produced from CBS – the sulphenamide studied here) seems to have insignificant effect on the overall cure rate.

Crosslink density : The crosslink density (determined by equilibrium swelling method) of gum compound containing varying levels of hydrofuramide is shown in Fig. 4. It can be seen that all the curves attain a maxima beyond which crosslink density decreases due to the well known phenomena of reversion. At the early stage of cure, the crosslink density is higher with compounds containing hydrofuramide as compared to the control compound. However, the maximum crosslink density is not significantly improved by the incorporation of hydrofuramide. Thus ultimate crosslink density is not influenced by the presence of hydrofuramide. These observations are in agreement with rheometric study where t_{max} is not improved by the incorporation of hydrofuramide although torque at the early stage of cure is higher with compounds containing hydrofuramide.

Free sulphur and crosslink efficiency : The rate of consumption of sulphur with time was determined by measuring free sulphur in the vulcanizate as a function of cure time. The plot of free sulphur content vs time of cure of gum compounds is shown in Fig. 5 Initially the rate of consumption of elemental sulphur is higher with compounds containing hydrofuramide. This is because the hydrofuramide promotes the decomposition of sulphenamide and hence vulcanization starts earlier

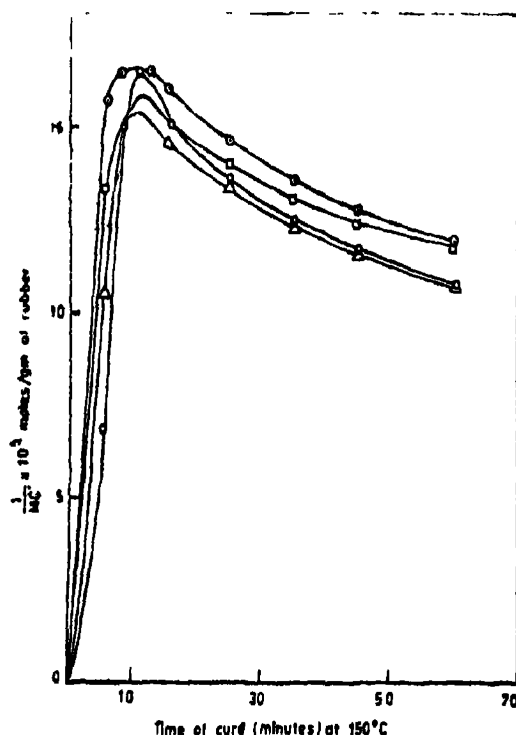


Fig. 4. Variation of crosslink density as a function of cure time.
Base formula : NR-100, ZnO-5, St. acid-2, CBS-0.8, S-2.5
O—No hydrofuramide   Δ—0.5 phr hydrofuramide
□—1 phr hydrofuramide   ⊙—2 phr hydrofuramide

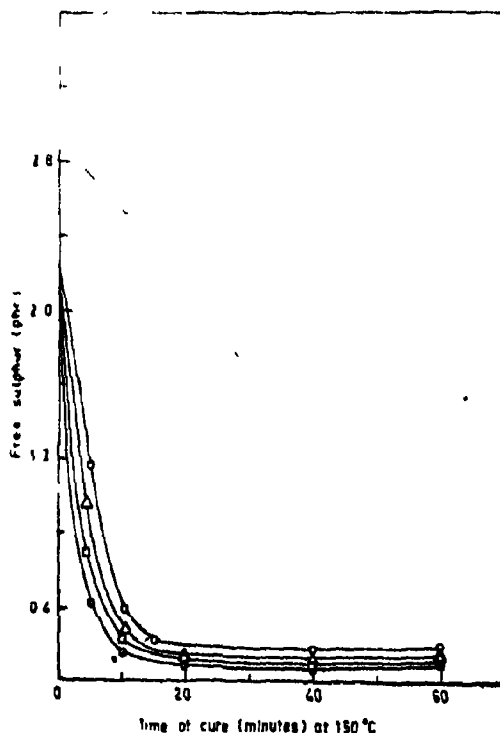


Fig 5. Free sulphur as a function of cure time.
Base formula : NR-100, ZnO 5, St acid-2, CBS-0.8, S-2.5,
O—0 phr hydrofuramide   Δ—0.5 phr hydrofuramide
□—1 phr hydrofuramide   ⊙—2 phr hydrofuramide

The consumption of sulphur apparently follows a first order rate law up to 20 min of cure time beyond which the plots follow a straight line pattern almost parallel to X-axis.

The efficiency of crosslinking was determined from the chemical crosslink density and combined sulphur as described earlier. In the early stage of cure although crosslinking efficiency was slightly higher with compounds containing hydrofuramide the efficiency at the optimum cure appears to be the same in all cases as can be seen from Table 3.

TABLE—3

Compound	Efficiency of vulcanisation
Control compound	15.0
Compound containing 0 5 phr hydrofuramide	15.6
Compound containing 1.0 phr hydrofuramide	15 0
Compound containing 2 0 phr hydrofuramide	14 8

Physical properties : The physical properties of gum compounds as well as N-330 (HAF) black filled compounds containing varying levels of hydrofuramide are shown in Tables 4 and 5. It can be observed from the tables that with the incorporation of hydrofuramide, tensile strength and ultimate

TABLE 4—PHYSICAL PROPERTIES OF GUM VULCANIZATES

Base formula : NR-100, ZnO-5 Stearic acid-2, CBS-0.8, S-2.5, Hydrofuramide-variable

Compound	1	2	3	4
Hydrofuramide (phr)	–	0 5	1.0	2.0
Tensile strength N/mm^2	22.5	22 6	2? 8	2? 8
Elongation at break %	650.0	660 0	660 0	675 0
300% Modulus N/mm^2	4.1	4.1	3.9	3.9
Hardness (IRHD)	45 0	45 5	46.5	46.5

elongation increases to some extent, whereas beyond 0.5 phr hydrofuramide 300% modulus decreases marginally with increasing levels of hydrofuramide.

TABLE 5—PHYSICAL PROPERTIES OF HAF (N-330) FILLED VULCANIZATE

Base formula : NR-100, HAF-50, ZnO-5, Stearic acid-2, CBS-0 8, S 2 5, Hydrofuramide-variable

Compound	5	6	7	8
Hydrofuramide (phr)	–	0 5	1.0	2.0
Tensile strength N/mm^2	24.0	24 2	24 4	24.5
Elongation at break %	450.0	450 0	460 0	475.0
300% Modulus N/mm^2	16 5	16.5	16 2	16.0
Hardness (IRHD)	73 5	73.5	74 5	75 0

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NOTES

Complexes of Pd(II) and Pt(II) with Some Organic Ligands

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THE complexes of Pt(II) display various physiological properties[1] and have been studied widely[2-4]. In the present communication I am reporting the preparation and characterisation of diacido complexes of Pd(II) and Pt(II) with 2-aminopyrimidine (AP) and 2-amino-4-methylpyrimidine (AMP) of formula $[M(AP/AMP)_2X_2]$ ($M = Pd^{2+}$ or Pt^{2+} and $X = Cl^-$, Br^-, I^-, NO_2^- or NCS^-) and neutral *bis* chelates $[ML_2]$ ($M = Pd^{2+}$ or Pt^{2+}) with LH=2-(*o*-hydroxyphenyl)imidazoline (HOPIMz)$_2$, -benzimidazole (HOPBz), -benzoxazole (HOPBOX) and -benzothiazole (HOPBT)

Preparation of complexes.

$[M(AP/AMP)_2Cl_2]$, ($M = Pd^{2+}$ or Pt^{2+}): An aqueous acidic solution of $PdCl_2$ (*p*H 3-4) was refluxed with an ethanolic solution of appropriate ligands (1 : 2.5 molar ratio) on a steam bath for a few minutes when a cream yellow precipitate of the dichloro complex separated gradually. In case of Pt(II)[5] the complex was obtained on concentration and cooling the refluxate to a small volume. The complexes were filtered, washed with water and dried in air.

$[M(AP/AMP)_2X_2]$, ($M = Pd^{2+}$ or Pt^{2+} and $X = Br^-$, I^-, NO_2^- or NCS^-): These complexes were prepared by refluxing an aqueous suspension of the dichloro complexes $M(AP/AMP)_2Cl_2$, ($M = Pd^{2+}$ or Pt^{2+}) with an excess of sodium or potassium salts of appropriate anions on a steam bath for about 2 hr. Palladium(II) complexes separated in hot, while Pt(II) complexes were obtained on concentrating the refluxate to a small volume and cooling.

$[ML_2]$, ($M = Pd^{2+}$ or Pt^{2+} and LH=HOPIMz, HOPBz, HOPBOX and HOPBT): An aqueous ethanolic solution of palladium(II) chloride was refluxed on a steam bath with appropriate ligand (about 1 : 2 molar ratio), by adjusting the *p*H of the reaction mixture with a dilute solution of NaOH to 5-6, for about half an hour when orange yellow or cream yellow complexes separated out gradually. In case of Pt(II) the *p*H of reaction mixture was raised to 8-9 by adding dilute solution of NaOH. The complexes separated when the refluxate was concentrated and *p*H was adjusted to 6-7 by adding dilute HCl. The products were filtered, washed with ethanol and dried in an air oven at 70-80°.

The results of elemental analysis of the complexes are in good agreement with proposed formulae.

Results and Discussion

The complexes of both Pd(II) and Pt(II) are diamagnetic, suggesting their square planar stereochemistry. The solid reflectance spectra of the complexes do not display distinct electronic bands rather they display a broad shoulder near 380-420 nm in Pd(II) complexes and at 370-380 nm in Pt(II) complexes assignable to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in square planar arrangement of ligand molecules around metal atoms[4]. The DMF solutions of the complexes are almost non-conducting ($\Lambda_M = 3-6$ ohm^{-1} mol^{-1} cm^2) supports their nonionic character.

IR spectra: From infrared spectral studies of the metal complexes of HOPIMz, HOPBz, HOPBOX and HOPBT the coordination of these ligands have been suggested through the deprotonated phenolic oxygen and tertiary nitrogen of imidazoline, -benzimidazole, -benzoxazole and -benzothiazole part of the ligand molecules[6,7]. The disappearance of (OH) stretching vibrations[6] of HOPIMz (2690 cm^{-1}), HOPBz (2540 cm^{-1}), HOPBOX (2280 cm^{-1}) and HOPBT (2260 cm^{-1}) suggests the bonding of the ligand molecules through deprotonated phenolic oxygen in these complexes. The (CN) stretching band of the ligands[6,7] in these complexes is shifted to lower frequencies by 10-32 cm^{-1} than those of the free ligands, as usually observed for N-bonded ligand having (CN) nitrogen of free ligand involved in strong hydrogen bonding[6-8]

2-Aminopyrimidine exhibits NH_2 symmetric stretch at 3170 cm^{-1} and asymmetric stretch at 3320 cm^{-1}. In complexes, the symmetric N-H vibration shifts to lower frequency by 20-60 cm^{-1} while asymmetric band splits into two medium bands observed at 3270-3300 and 3390 $\pm$ 10 cm^{-1} respectively. The (N–H) symmetric stretch of AMP located at 3160 cm^{-1} also shifts to lower wave number by 10-30 cm^{-1} and asymmetric stretch (3335 cm^{-1}) splits into two bands in its complexes and observed at 3430$\pm$10 and 3340$\pm$10 cm^{-1}. The N–H degenerate deformation vibration of AP (1482 cm^{-1}) as well as of AMP (1470 cm^{-1}) is raised to higher wave number by 10-25 cm^{-1} in most of the complexes. Thus, the lowering of ν_s(NH) band and the blue shift of (N–H) deformation vibrations suggest the coordination of ligand molecules through amino nitrogen in these complexes[9]. The splitting of $\nu_{as}(NH_2)$ band can

be attributable to *cis* bonding of ligand molecules in the complexes.

The ir spectra of $[M(AP/AMP)_2(SCN)_2]$ ($M=Pd^{2+}$ or Pt^{2+}) exhibit a strong and sharp band at 2115-2122 cm^{-1} and weak band at 2035-2100 cm^{-1} (Table 1) attributable to $\nu(C=N)$ stretch of coordinated thiocyanate group[10-11]. The $\nu(C=S)$ stretching band located near 680-710 cm^{-1} (Table 1)

TABLE—1

Complexes	$\nu(C=N)$ in cm^{-1}	$\nu(C=S)$ in cm^{-1}
$[Pd(AP)_2(SCN)_2]$	2120 s. sp 2070 w	680 w
$[Pd(AMP)_2(SCN)_2]$	2115 s sp 2035 w	710 w
$[Pt(AP)_2(SCN)_2]$	2122 s sp 2100 w	705 w
$[Pt(AMP)_2(SCN)_2]$	2118 s. sp. 2030 w	710 w

indicates the S-bonding of thiocyanate group in these thiocyanato complexes[12,13]. The bonding of thiocyanate group through sulphur atom in complexes is consistent with class 'b' character of Pt(II) and Pd(II).

In the ir spectra of $[M(AP/AMP)_2(NO_2)_2]$ ($M=Pd^{2+}$ or Pt^{2+}) the $\nu_{as}(NO_2)$ as well as $\nu_s(NO_2)$ vibration is raised to higher frequencies (Table 2)

TABLE—2

Compound	$\nu_{as}(NO_2)$ in cm^{-1}	$\nu_s(NO_2)$ in cm^{-1}	$\delta(ONO)$ in cm^{-1}
$[Pt(AP)_2(NO_2)_2]$	1400 vs br	1305 vs 1258 s	885 s
$[Pt(AMP)_2(NO_2)_2]$	1415 s. br	1335 vs 1270 s	890 s
$[Pd(AP)_2(NO_2)_2]$	1405 vs. br	1340 s 1275 s	828 s
$[Pd(AMP)_2(NO_2)_2]$	1400 vs. br	1318 s 1292 s	898 s 818 s

vs = very strong, br = broad and s = strong.

suggesting that NO_2 group is coordinated through nitrogen atom in these complexes[14]. The $\nu_s(NO_2)$ vibration of the complexes has been found to split into two bands similar to *cis* bonded nitro group in square planar dinitro complexes[15].

Thus, on the basis of above results it is inferred that in diacido complexes $M(AP/AMP)_2X_2$ ($X=Cl^-$, Br^-, I^-, NO_2^- or SCN^- and $M=Pd^{2+}$ or Pt^{2+}), the anions are bonded in *cis* position and ligands are coordinated to metal atom through amino nitrogen as unidentate molecules.

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Molecular Complex of 8-Hydroxyquinoline and Potassium Hexacyanoferrate(II) in Acid Medium

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SAHA and Saha[1] described the molecular complexes of 8-hydroxyquinoline (oxine) and potassium hexacyanoferrates(II and III) respectively prepared in dilute aqueous acetic acid medium; the compositions of the complexes were given as $K_4Fe(CN)_6.2$ oxine and $K_3Fe(CN)_6$ 2 oxine respectively. A glance at the formulae given raised some doubt in our mind as to what could be the binding forces to make the complexes so stable and we decided to study the first complex independently.

Experimental

All chemicals used in the work were of AnalaR/GR quality The complex was prepared following the method[1] by dissolving 10.0 g $K_4Fe(CN)_6.3H_2O$ in 30 ml of water and 6 85 g of oxine in 37 ml of dilute (5 *M*) acetic acid, and mixing the two solution with stirring; the chocolate coloured complex formed immediately was filtered in sintered gooch crucible, washed with water and dried in vacuum desiccator over KOH; yield 9.0 g. No HCN liberated during the preparation of the complex.

Results and Discussion

In contrast to the belief of Saha and Saha, the complex does not contain any appreciable amount of potassium (<0.01%) and does not give the flame test for potassium. This result leads one to believe that the complex is formed between hexacyanoferric(II) acid $[H_4Fe(CN)_6]$ and oxine. To have an

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idea about the composition of the complex, increasing amounts of oxine solution in 5 *M* acetic acid were separately added to a fixed amount of potassium hexacyanoferrate(II) solution in water so that the oxine/hexacyanoferrate molar ratios varied from one to seven. The complex formed in each case was collected in previously weighed sintered gooch crucible, washed with water, dried in vacuum to constant weight and yield recorded. The results are depicted in the curve A of Fig. 1. The results indicate that the complex has the oxine to hexacyanoferrate(II) ratio 4 : 1. The theoretical yields calculated on the assumption of the composition $H_4Fe(CN)_6$. 4 oxine . $3H_2O$ (which is confirmed later) is shown in the curve B of the same figure. These two curves not only indicate the composition speculated to be reasonable, but also shows that in the preparation of the complex the yield is almost quantitative and not 70% as reported by the previous authors. The reason for 70% yield is presumably due to the use of proportionately less amount of oxine in their preparation.

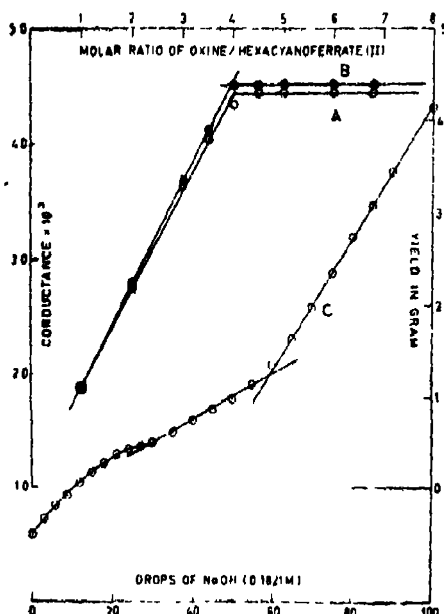


Fig. 1. A. Yield in g of the complex formed by adding separately varying amounts of 16.9% oxine solution in 5 *M* acetic acid to 7.50 ml of solution containing 2.16 g of $K_4Fe(CN)_6.3H_2O$ in water.
B. Theoretical yield of the complex based on the composition $H_4Fe(CN)_6.4Ox.3H_2O$ of the complex.
C. Conductometric titration of 50.0 mg of the complex by 0.182 *N* NaOH solution.

Conductometric titration of the complex by alkali was also done to verify the composition derived from the results mentioned. The complex will be acidic with eight protons [four from hexacyanoferric(II) acid and four from oxine] per molecule. Curve C of Fig. 1 shows the titration curve obtained by titrating a suspension in 30 ml water of 50.0 mg of the complex with 0.182 *N* NaOH. The titration curve has two breaks at 30 and 59.5 drops (1.29 and 2.59 ml) of alkali, and the equivalent weight works out to be 107.3, and hence the molecular weight of the complex 858.4 which is very close to 850.7, the calculated molecular weight of the complex. The two breaks at 1 : 1 volume of the alkali also supports the proposed composition of the complex. The non-linear increase in conductance leading to the first break may be due to the different *p*Ks of $H_4Fe(CN)_6$ as well as to the progressive solubilisation of the complex during the titration. The chocolate colour of the complex vanishes at 30 drops of alkali indicating that with conversion of $H_4Fe(CN)_6$ to $Na_4Fe(CN)_6$ the complex breaks up into the components. The subsequent linear increase leading to the second break reflects the titration of oxine.

Finally, the element analyses results also confirm the formula $H_4Fe(CN)_6$. 4 oxine . $3H_2O$. Found : C, 58.83 ; H, 4.81 ; O, 13.33 ; N, 16.48 ; Fe, 6.63. Calcd. ; C, 59.30 ; H, 4.50 ; O, 13.17 ; N, 16.47 ; Fe, 6.57%. It is to be pointed out that Saha and Saha gave the figures for N (16.75) and Fe (8.54) of which figure for iron is distinctly different from our estimation.

Conclusion : The complex formed between oxine and potassium hexacyanoferrate(II) in acidic medium is very similar to potassium hexacyanoferrate(II) with the potassium ions replaced by protonated oxine cations $[OxH^+]$, and the complex should better be represented as $[OxH^+]_4$-$[Fe(CN)_6]^{4-}.3H_2O$. The electrostatic binding between the hexacyanoferrate(II) anion and the protonated oxine cations makes this compound stable towards heat. The yield in the preparation of the complex is almost quantitative and hence this may give a potential method of the estimation of oxine or hexacyanoferrate.

Acknowledgement

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Electromigration of Some Metal Ions on Filter Paper using Aqueous Glycolate Buffer Media

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THE work on separation of metal ions by electromigration on filter paper has been reviewed by Bailey and Yaffe[1] quite adequately. Complexing

agents of various types have been used for separating transition and inner-transition metal ions[2-9]. Attempts have been made to use glycolic acid as its aqueous solution to provide potent complexing media for such studies and the results are presented here. As the pH of the electrolyte plays an important part in modifying the migration trends of metal ions, the use of suitably buffered solutions at fixed pH values have been done to study the electromigration of some 14 metal ions by horizontal electrophoretic method.

Experimental

Aqueous 1.14, 2, 4, 5 and 7% (w/v) solutions of glycolic acid (Riedel, W Germany) were prepared and used as electrolytes at definite pH values. The pH of these solutions was adjusted with ammonia solution using a pH meter.

Stock solutions (0.1 M) of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ag^{+}, Tl^{+}, Th^{4+}, UO_2^{2+} as nitrate and Ti^{4+}, Mn^{2+}, Hg^{2+}, Zn^{2+} as chlorides were prepared from A.R. reagents. Working solutions containing 3-10 $\mu g/\mu l$ were prepared by dilution.

The chromogenic reagents employed for detection of metal ions were (a) rubeanic acid, (b) alizarin red-S, (c) chromotropic acid, (d) rubeanic acid/salicylaldoxime/alizarin mixture, (e) yellow ammonium sulphide and (f) potassium ferrocyanide.

Whatman No. 1 filter paper strips of 2 cm × 35 cm were used for electromigration of metal ions at 5V/cm potential gradient for 2 hr. Many separations have been carried out successfully in aqueous glycolic acid media suitably buffered. These have been reported in Table 1.

TABLE 1—SEPARATION OF TERNARY, QUATERNARY AND POLYNARY METAL ION MIXTURES

Electrolyte % w/v	Mixture	Position on paper strip		
		Cationic (−)	Iso-electric	Anionic (+)
Glycolic acid (aq.) 1.14% at pH 2	Fe-Co-Cu	Co Cu Fe		
	Fe-Ni-Cu	Ni Cu Fe		
	Fe-Co-Ag	Co Fe	Ag	
	Fe-Ni-Ag	Ni Fe	Ag	
	Fe-Cu-Ag	Cu Fe	Ag	
	Ni-Cu-Ag	Ni Cu	Ag	
	Co-Cu-Ag	Co Cu	Ag	
Glycolic acid (aq.) 4% at pH 2	Ti-Fe-Co	Co Fe Ti		
	Ti-Fe-Ni	Ni Fe Ti		
	Ti-Fe-Cu	Cu Fe Ti		
	Ti-Fe-Cd	Cd Fe Ti		
	Ti-Fe-Hg	Fe Ti		Hg
	Ti-Fe-UO_2	UO_2 Fe		Ti
	Ti-Co-Cu	Co Cu Ti		
	Ti-Co-Hg	Co Ti		Hg
	Ti-Ni-Cu	Ni Cu		Ti
	Ti-Cu-Hg	Cu Ti		Hg
	Ti-Ni-Hg	Ni Ti		Hg
	UO_2-Co-Hg	Co UO_2		Hg
	UO_2-Ni-Hg	Ni UO_2		Hg
	UO_2-Cu-Hg	Cu UO_2		Hg

Table 1 (Contd.)

Glycolic acid (aq.) 4% at pH 2	Tl-Fe-Cu-Hg	Cu Fe Tl		Hg
	Tl-Fe-Cu-Ag-Hg	Cu Fe Tl	Ag	Hg
	Tl-Fe-Co-Cu-Hg	Co Cu Fe Ti		Hg
	Tl-Fe-Ni-Cu-Hg	Ni Cu Fe Tl		Hg
	Hg-Tl-Fe-Co-Cu-Ag	Co Cu Fe Tl	Ag	Hg
	Ti-Fe-Ni-Cu-Ag-Hg	Ni Cu Fe Tl	Ag	Hg
Glycolic acid (aq.) 2% at pH 4	Fe-Ti-Mn	Mn		Fe Ti
	Tl-Pb-Hg	Tl Pb	Pb	Hg
	Ag-Tl-Hg	Tl	Ag	Hg
Glycolic acid (aq.) 2% at pH 6	Mn-Fe-Zn	Mn		Fe Zn
	Tl-Pb-Hg	Tl Pb	Pb	Hg
	Ag-Tl-Hg	Tl	Ag	Hg
Glycolic acid (aq.) 5% at pH 6	Fe-Mn-Zn	Mn	Fe	Zn
	Tl-Pb-Hg	Tl	Pb	Pb Hg
	Ag-Tl-Hg	Tl	Ag	Hg

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Kinetics of Oxidation of L-Rhamnose by Vanadium(V)

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KINETICS of oxidation of hexoses[1-3] and pentoses[4] by vanadium(V) have been reported earlier. We are now reporting that of L-rhamnose, a deoxy sugar, in sulphuric acid medium.

Experimental and Results

The kinetics of reaction has been studied under the condition [L-rhamnose] and $[H_2SO_4] \gg$ [vanadium(V)]. Other details are the same as described earlier[4].

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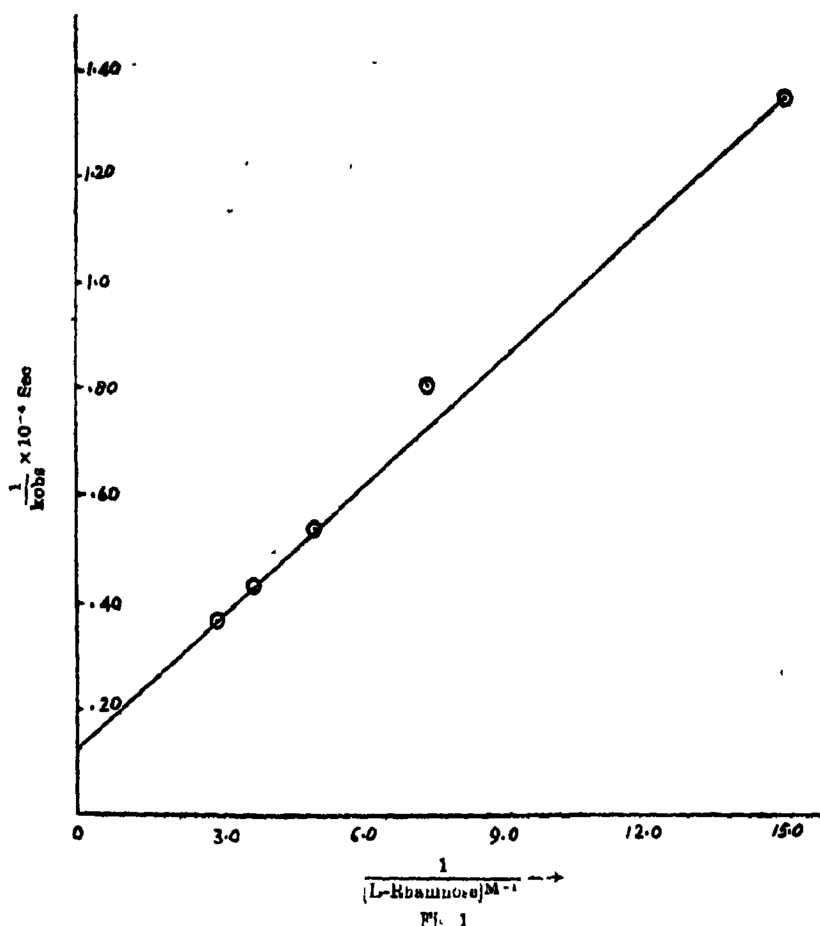


Fig. 1

Variation of pseudo first order rate constant k_1 (sec^{-1}) with [L-rhamnose] and [H_2SO_4] is given in Table 1.

TABLE 1 – VARIATION OF k_1 WITH L-RHAMNOSE] AND [H_2SO_4] AT 65° VANADIUM(V) = $6\cdot0\times10^{-3}$ M

[L-Rhamnose] × 10 M	[H_2SO_4] M	$k_1\times10^4$ sec^{-1}
0.66	1 25	0 75±0.08
1.33	1.25	1 24±0 11
2.00	1.25	1.84±0 17
2.66	1.25	2.31±0.12
3 33	1.25	2.77±0.22
0.66	0 10	0.42±0.07
0.66	1.25	0.75±0 03
0.66	2.39	1.16±0.08
0.66	3.69	1.87±0 04
0.66	4.68	2.17±0 14
0.66	5.82	3 06±0.12
0.66	6.99	4 84±0.34

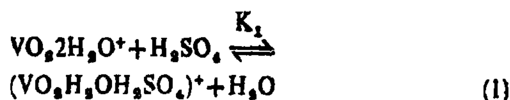
A plot of $1/k_1$ against 1/[L-rhamnose] gives a straight line with an intercept (cf Fig. 1) suggesting the complex formation between vanadium(V) and L-rhamnose. The value of equilibrium constant K has been computed as 1.61×10^4. k_1 depends on [H_2SO_4] as 1.07 slope value is obtained from log k_1 and log [H_2SO_4] plot. Zucker-Hammett[5], Bunnett[6] and Bunnett-Olsen[7] plots were obtained with slope values as −0.27, 4.3 (w) and 0.98 (ϕ) respectively. k_1 has also been found to increase from 0.42×10^{-4} sec^{-1} to 6.29×10^{-4} sec^{-1} when % composition of acetic acid-water mixture was varied from 0-60% at [vanadium(V)] = 6.0×10^{-3} M, [L-rhamnose] = $6\cdot0\times10^{-2}$ M, [H_2SO_4] = 0.10 M and temperature 65°

From the variation of k_1 with temperature, the thermodynamic parameters are obtained as :

$\Delta H^{\neq} = 26.76\pm0.09$ Kcal $mole^{-1}$, $\Delta S^{\neq} = 1.98\pm0.23$ e.u. and $\Delta G^{\neq} = 26.04\pm0.20$ Kcal $mole^{-1}$

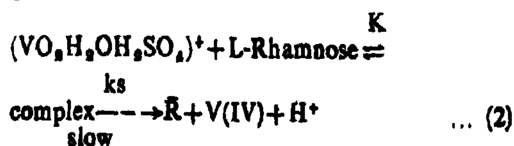
Discussion

Vanadium(V) exists as $VO_2 2H_2O^+$ or $V(OH)_4^+$ in acidic medium[8]. The active species formation can be expressed as[9]



$$VO_2 2H_2O^+ + H_2SO_4 \overset{K_1}{\rightleftharpoons} (VO_2H_2OH_2SO_4)^+ + H_2O \quad (1)$$

The following reaction steps can now be proposed :



$$(VO_2H_2OH_2SO_4)^+ + \text{L-Rhamnose} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow[\text{slow}]{k_s} \dot{R} + V(IV) + H^+ \quad \ldots (2)$$



$$\dot{R} + V(V) \xrightarrow[\text{fast}]{kf} \text{Products} \quad (3)$$

{here $\dot{R}$ = free radical (confirmed by induced poly- ıerisation with acryl nitrile) and kf ≫ ks

The final rate law thus can be derived as :

$$-\frac{d[V(V)]}{dt} = \frac{2ksK_1K[VO_2 2H_2O^+][\text{L-Rhamnose}][H_2SO_4]}{1+K[\text{L-Rhamnose}]} \quad (4)$$

Due to coordination, the activation energy for -C bond rupture is lowered[10] and this is in ¿reement with the observed value of $\Delta H^{\neq}$. urther, the unimolecular disproportion of complex roposed in step 3 is consistant with the observed mall value of $\Delta S^{\neq}$.

Thus, the proposed steps (1-3) and rate law (4) ıcorporate the kinetic results satisfactorily

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Potentiometric Determination of Dissociation Constants of DL-Tryptophan in Different Aquo-Organic Solvents

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IN continuation of our earlier work on metal-amino acid complexes[1,2], this communication reports the dissociation constant (pK) of DL-tryptophan at constant ionic strength in different aquo-organic solvents (20%, v/v) viz, acetone, acetonitrile, iso-propanol, N,N-dimethyl formamide, *n*-butanol and dimethyl sulfoxide by Albert Serjeant[3] method.

Experimental

DL-Tryptophan was obtained from BDH and all other solvents were of AnalaR grade. pH measurements were made on a Toshniwal digital pH meter (accuracy ± 0.1 pH) with glass calomel electrode assembly The temperature of the cell was maintained by a thermostat (U_1-type, German) having an accuracy of ± 0.1°.

For determining the pK of DL-tryptophan (HA) the calculated amount of the HA corresponding to 0.01 *M* per 25 ml solution is dissolved in 20% solvent and 0.1 *M* $NaClO_4$ (giving a total volume of 22.5 ml). It was titrated against 0.1 *M* NaOH in an inert atmosphere of nitrogen and the pH was recorded as equilibrium reached after each addition[3] The pK values of $\overset{+}{N}H_3CHCOO^-$ group of DL-tryptophan determined in different solvents (20%, v/v) at 25 ± 0.1 and $\mu = 0.1$ *M* $NaClO_4$ are given in Table 1 and follow the order N,N-dimethyl formamide (9.24) > dimethyl sulfoxide (9.19) > acetone (9.15) > iso-propanol (9.14) > acetonitrile (9.08) > water (9 02) > *n*-butanol (8.96).

This variation in values may be partly due to the change in dielectric constant[4] of the medium which depends on the viscosity and ionic interaction in solutions[5].

Table 1—The pK Values of DL-Tryptophan in Different Solvents (20%, v/v) at 25°±0 1 and μ=0.1 *M* $NaClO_4$

Titrant 1*N*	A		B		C		D		E		F		G	
NaOH ml	pH	pK	pH	pK	pH	pK	pH	pK	pH	pK	pH	pK	pH	pK
0.0	6.75	–	5.70	–	6.48	–	6.04	–	6 60	–	5.95	–	4.60	–
0 5	8 57	9.17	8.45	9 05	8.45	9.05	8.44	9.04	8.37	8.97	8 34	8.94	8 32	8.92
1.0	9.00	9 17	8.98	9.16	8.90	9 07	8.89	9 07	8.86	9.04	8.81	8.98	8 82	8.96
1.5	9.37	9.20	9.32	9.15	9 27	9.10	9 27	9.10	9 28	9.11	9.18	9.2[illegible]	9 20	9.03
2.0	9 76	9.20	9.72	9.15	9.70	9.13	9.67	9.10	9 70	9.13	9.59	9.02	9 55	8.98
2.5	10.48	9.48	10.45	9.45	10.40	9.40	10.38	9 39	10.48	9.15	10.22	8.91	10.23	8.94
Mean	–	9.24	–	9.19	–	9.15	–	9.14	–	9.08	–	9.02	–	8.96

A=N, N-dimethyl formamide ; B=dimethyl sulfoxide ; C=acetone ; D=iso-propanol , E=acetonitrile , F=water , G=*n*-butanol.

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*p*H-Metric Studies on the Copper Benzamido-thiosemicarbazide Complex

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INTERACTION between thiosemicarbazide, $NH_2C(X)NHNH_2$ (X = O, S, Se) and Pb(II) has been reported by Ajayi *et al*[1] and stability constants were calculated by polarographic method. Stability constant and heat of formation of Hg(II) complex of thiosemicarbazide were determined by Goddard and coworkers[2]. Campbell and Grezeskowiak[3] prepared two series of Cu(II) complexes of thiosemicarbazide and elucidated their structure employing ultraviolet and visible spectroscopic technique. In our earlier communication[4], extensive studies on the interaction of Hg(II), Cu(II) and Pb(II) with benzamidothiosemicarbazide in solution and in solid state were reported.

In the present communication, *p*H-metric results of our studies on the composition as well as the stepwise stability constant and overall stability constant of benzamidothiosemicarbazide (abbreviated as BTSC) complex of Cu(II) have been reported.

Experimental

Benzamidothiosemicarbazide (BTSC) was prepared by the method described by Verma[5] and its solution was prepared by dissolving weighed amounts in 80 : 20 ethyl alcohol : water mixture. Fresh solution of BTSC was always used. Stock solution of copper acetate was prepared by dissolving the salt (B. D. H., 'AR' grade) in doubly distilled CO_2 free water. The strength of the solution was determined by the usual method. Fresh solution of aqueous KOH (B. D. H., 'AR' grade) was always used. Elico-*p*H meter, in conjunction with hydrogen glass electrode and S. C. E. was used for *p*H measurements. Standard solution of potassium hydroxide was added to the reagent vessel from microburette (least count 0.05 ml). All the *p*[H] measurements were performed at 29°±0.1 usi[ng] Toshniwal model thermostat.

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Results and Discussion

Bjerrum's method has certain limitations wh[en] applied to aqueous-mixed alcoholic medium wi[th] more than 50 per cent alcohol, since the *p*H-sca[le] set for aqueous medium is not applicable to no[n-]aqueous medium. The values of stability consta[nts] determined for these systems would not, therefo[re] be the real values but would be the apparent on[es]. But here, since the studies were carried out [in] alcohol-water mixtures with more than 50 per ce[nt] water, the stability constants determined may [be] taken as real values.

The *p*K value (8.1) of BTSC determin[ed] *p*H-metrically, was in close agreement with t[he] value obtained by polarographic method[6]. *p*[H-]metric titrations performed with mixtures of met[al] ligand, ligand and metal separately against 0.1 KOH showed lowering of *p*H, proving liberati[on] of H^+ ions as a result of complex formation. Ma[xi]mum lowering of *p*H in the case of 1 : 2 Cu-BTS[C] mixture and the inflection corresponding to 2 mo[les] of KOH : 1 mole of copper acetate indicated 1 : [2] metal-ligand ratio in the complex.

*p*H-metric titration of BTSC alone and in t[he] presence of different concentration of Cu^{2+} io[ns] performed according to the method recommend[ed] by Calvin and Melchoir[7], gave typical *p*H-met[ric] curves when titrated against standard KOH. Fr[om] these curve at various valuess of *p*H, a set of $\bar{n}$ valu[es] was determined and the concentration of free liga[nd] ($\bar{A}$) was calculated. The values of $\bar{n}$ were plott[ed] against the corresponding values of *p*A or −log(A). As a first approximation the value of *p*A at $\bar{n}$=[0.5] and at $\bar{n}$=1.5 are equal to log K_1 (3.703) and l[og] K_2 (3.037) respectively. The overall stability co[ns]tant (log K) came to be 6.740.

These temporary constants were corrected [by] Bjerrum's method[8] of successive approximati[on]. The value of spreading factor 'x' was found to [be] 1.0765 and the corrected values of formation fu[nc]tion ($\bar{n}$) for each corresponding value of ($\bar{A}$) we[re] then plotted against −log (A). The final values log K_1 = 3.85, log K_2 = 2.90 and overall log K = 6.[...] were obtained.

From the results it is clear that $\bar{n}$ increases wi[th] the increase in *p*H showing thereby that it is t[he] anionic form which takes part in the reaction.

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A Dynamic TG Study of *Bis* (acetylacetonato)-Copper(II)

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THE thermal decomposition of *bis*(acetylacetonato)-copper(II), $[Cu(acac)_2]$, has been studied by dynamic thermogravimetry. The compound has been reported to be stable and non-volatile[1] upto 191° and to decompose at higher temperatures in the absence of air to acac and metallic copper[2] In the present investigation carried out in static air, the residue left behind has been shown to be CuO by analysis. In this dynamic TG study, the fractional decomposition values (αs) were employed in studying the kinetics of the overall decomposition process by methods described elsewhere[3,4,5]. Different functional forms of α, viz $f(\alpha)$s, assumed to govern the rate controlling process, were chosen for obtaining the $g(\alpha)$ values (where $g(\alpha)=\int_0^{\infty}\frac{d\alpha}{f(\alpha)}$) from rate law $\frac{\alpha d}{dt}=k\,f(\alpha)$. These $g(\alpha)$ values were used to evaluate the kinetic parameters.

Dynamic TG traces of the pure and dry complex (125 mg; mesh 200-240) prepared by known methods[6] were obtained using 'Stanton' recording thermobalance (Model TR-I). The heating rate was 4° min^{-1}.

The TG trace redrawn as mass of sample versus temperature and the DTG curve are given in Fig. 1. The temperature of inception, T_i, temperature of completion, T_f, and peak temperature of decomposition, T_s, are 463, 538 and 524 K respectively. Mass loss found for the decomposition (95 mg) at T_f was in excellent agreement with the theoretical requirement (94.6 mg). Plots were made, $g(\alpha)$ versus temperature, for different mechanistic models for the decomposition and are set out in Fig. 2. From the linear portion of such plots, (i.e. 5, 6 and 7 in the figure) the frequency factor, Z, activation energy E* and entropy of activation ΔS^* were calculated by methods described elsewhere[4,7] and are presented in Table 1. Although three model

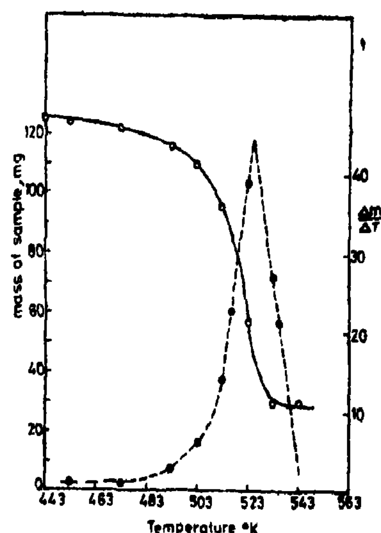
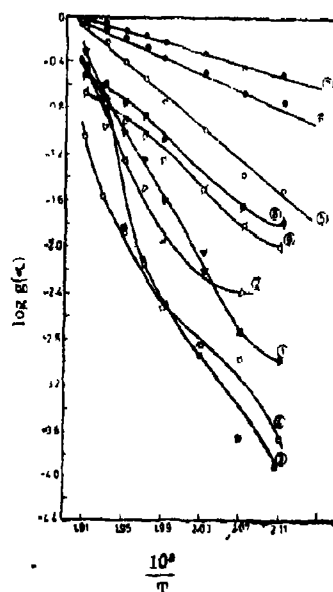


Fig 1 TG, DTG curves.
O-TG, ●-DTG



$\frac{10^4}{T}$

Fig. 2 Mechanistic plots.
$g(\alpha)$: ▲α^2, △$\alpha+(1-\alpha)\ln(1-\alpha)$, ■$[1-(1-\alpha)^{1/3}]^2$, □$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$, O$-\ln(1-\alpha)$, ●$[-\ln(1-\alpha)]^{1/2}$, ⊖$[-\ln(1-\alpha)]^{1/3}$ ● $1-(1-\alpha)^{1/2}$ O $1-(1-\alpha)^{1/3}$

TABLE 1—KINETIC PARAMETERS

Form of $f(\alpha)$	$g(\alpha)$	Frequency factor Z	Energy of activation, E* (k. J. mole^{-1})
$(1-\alpha)$	$-\ln(1-\alpha)$	7.9×10^{10}	184.8
$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	5.6×10^{8}	64.9
$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	2.6×10^{5}	41.4

equations for $g(\alpha)$ viz. $-\ln(1-\alpha)$, $[-\ln(1-\alpha)]^{1/2}$ and $[-\ln(1-\alpha)]^{1/3}$ gave linear relations, only the one corresponding to the Mampel model equation[8], i.e. $(1-\alpha)$ for $f(\alpha)$, gave reasonable values of frequency factor and activation energy. The order of magnitude of frequency factor according to this model equation is agreeably close to theoretical requirement[9]. The moderately negative entropy of activation (-71 JK^{-1} $mole^{-1}$) indicates formation of an ordered transition state. It is likely that the complex decomposes by random nucleation, i.e. with formation of a nucleus on every particle

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Studies on Schiff Bases of Veratraldehyde

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A survey of literature[1-8] showed that study of Schiff bases of veratraldehyde has not been carried out so far It was, therefore, of interest to synthesize new Schiff bases derived from veratraldehyde. This paper describes the synthesis of veratraldehyde Schiff bases, their sodium borohydride reduction products, spectral studies of the Schiff bases and their reduced products, and fungicidal activity of Schiff bases and the secondary amines.

The Schiff bases have been prepared in quantitative yields by condensing equimolar quantities of veratraldehyde and aromatic amines (aniline and substituted anilines) in toluene by azeotropic distillation of water formed during the reaction. The Schiff bases having m-NO_2 and o-OCH_3 groups are dark coloured thick oils.

The uv spectra of the Schiff bases give four absorption bands at 213, 235, 270 and 335 nm. It has been found that the absorption bands (band II at 235 nm and band IV at 335 nm) are sensitive to N-phenyl substitution while the other two bands (band I at 213 nm and band III at 270 nm) usually remain unaffected. Band at ~270 nm is the characteristic band of $>C=N-$ as is shown by the fact that this band completely disappears on reduction of the $>C=N-$ linkage with sodium borohydride. In ir, $>C=N-$ absorption is observed at ~1625 cm^{-1}.

Reduction of veratraldehyde Schiff bases has been carried out with sodium borohydride in methanol at 60-65°. The use of higher temperature is partly required because of low solubility of the Schiff bases in methanol. The reduction is not possible in case of Schiff bases having hydroxyl group in the N-phenyl ring and it is suppressed in case of 3,4-dimethoxybenzal-o-anisidine because of steric hindrance

A study of the spectra of the reduced products in conjugation with those of the parent Schiff bases reveals that the absorption bands assigned to $>C=N-$ linkage (~270 nm) are absent in the spectra of the reduced products. The ir spectra of the dihydro products lack the absorption bands (~1625 cm^{-1}) assigned to $>C=N-$ but contain additional bands (3440-3420 cm^{-1}) due to NH group.

The Schiff bases and their reduced products as well as the uv spectra of the Schiff bases are recorded in Table 1

TABLE 1—CHARACTERISTICS OF VERATRALDEHYDE SCHIFF BASES AND THEIR DIHYDRO PRODUCTS

Sl No	Substituent in N-phenyl ring	m p (°C) of Schiff Base	m p (°C) of Dihydro Product	UV Spectra of the Schiff Bases of Veratraldehyde: Band I MeOH λ_{max}(nm)(log ε)	Band II MeOH λ_{max}(nm)(log ε)	Band III MeOH λ_{max}(nm)(log ε)	Band IV MeOH λ_{max}(nm)(log ε)
1	H	83	92	213 (4.09)	235 (4.28)	268 (4.39)	335 (4.39)
2	m-CH_3	115	87	209 (4.18)	– –	270 (4.16)	337 (3.04)
3.	p-CH_3	99	110	210 (3.85)	231 (4.12)	267 (4.38)	345 (4.35)
4.	p-OCH_3	126	137	211 (4.30)	242 (4.16)	269 (4.36)	350 (4.30)
5	p-OC_2H_5	97	60	211 (4.30)	242 (4.16)	270 (4.44)	350 (4.40)
6.	o-OH	100	–	203 (4.62)	242 (4.32)	263 (3.34)	355 (3.64)
7.	m-OH	215	–	210 (4.34)	248 (4.38)	270 (4.31)	355 (3.63)
8.	m-Cl	80	123	211 (3.85)	– –	268 (3.85)	330 (3.15)
9.	p-Cl	83	124	211 (3.45)	– –	268 (4.37)	336 (4.31)
10.	p-Br	99	107	210 (4.34)	– –	270 (4.44)	346 (4.32)
11.	o-OCH_3	oil	100	209 (4.21)	230 (4.10)	269 (4.40)	348 (4.30)
12.	m-NO_2	oil	141	– –	– –	268 (5.54)	– –

All the melting points are uncorrected All the compounds gave satisfactory elemental analyses and yields were excellent

The 3,4-dimethoxybenzalanilines were subjected to *in vitro* activity test against various fungi. The Schiff bases having electron-donating substituents in the N-phenyl ring have shown remarkable activity against the fungi *Alternaria solani* and *Colletotrichum capsici*. Similar test of secondary amines have indicated that though they are active against the above mentioned fungi, they are less effective than the Schiff bases.

Experimental

Synthesis of 3, 4-dimethoxybenzalaniline : A mixture of veratraldehyde (0.1 mole), aniline (0.1 mole) and toluene (125 ml) was refluxed till water (0.1 mole) had separated out. Distillation of the solvent gave a crude Schiff base which was recrystallised from methanol as white shining crystals, m.p. 83° (yield 100%).

Reduction of 3, 4-dimethoxybenzalaniline : To a stirred solution of 3,4-dimethoxybenzalaniline (0.1 mole) in methanol (50 ml) was added an alkaline solution of sodium borohydride (2 0 g in 2 ml of 2 *N* NaOH diluted to 20 ml with distilled water) dropwise at a rate so as to keep the temperature between 50-60°. The contents were then cooled and kept overnight at room temperature. The excess of solvent was distilled off, the contents were cooled, diluted with water (100 ml), chilled in ice bath for 2 hr and filtered. The crude product was then recrystallised from methanol to give light yellow shining needles, m.p. 92° (yield 80%).

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Synthesis of 9-Alkyl-6-Mercaptopurine Analogues

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6-MERCAPTOPURINE (6MP)[1], an antimetabolite with relatively low toxicity is widely used clinically to treat leukemia. The activity of 6MP substituted at the 9-position with normal alkyl and cycloalkyl groups were studied[2] earlier against a line of H. Ep2 cells and two sublines resistant to 6MP. It was found that the butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl and octyl derivatives exerted inhibitory effect on all the 3 lines. Friend Leukemia virus infection in mice was inhibited by 9-cyclopentyl-6-mercaptopurine[3]. It was of interest to study the effect of long chain alkyl substitution at 9-position of 6MP on tumour as it was observed that lipophilicity sometimes increased the activity of an anticancer drug when it could be modified by appropriate substitution[4]. This communication describes the synthesis of 9-undecyl (I), dodecyl (II), tetradecyl (III), hexadecyl (IV) and octadecyl 6-mercaptopurine (V) and studies on their effect *in vitro* against KB cells and *in vivo* against lymphoid leukemia L1210 and Sarcoma-180.

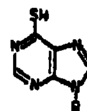


Fig 1. I R=$C_{11}H_{23}$, II. R=$C_{12}H_{25}$, III. R=$C_{14}H_{29}$; IV. R=$C_{16}H_{33}$, V R=$C_{18}H_{37}$

The above 6MP analogues were prepared by reacting thiourea in *n*-propanol with the corresponding 6-chloro-9-alkyl purines whose synthesis has been reported earlier[5].

Experimental

The melting points were determined in open capillary tubes using a Thomas-Hoover Unimelt apparatus and are uncorrected. The ultraviolet spectra in ethanol and the infra red spectra in KBr were recorded in Pye Unicam SP8 100 and Perkin Elmer 177 spectrophotometer respectively. The experimental procedure being similar, the preparation of 9-undecyl 6-mercaptopurine is described here as a representative case.

6-Mercapto-9-undecyl purine (I) : A solution of 322 mg (1.04 mmole) of 6-chloro-9-undecyl purine[5] and 100 mg (1.32 mmole) of thiourea in 10 ml *n*-propanol was heated under reflux for 1 hr and then cooled in ice bath. The precipitated solid was collected by filtration, washed with cold *n*-propanol and dried ; yield 230 mg (72 0%), m p. 260-64°. Two crystallisations of the crude material from ethanol gave the analytical sample (I), m p 265-66°. λ_{max} in nm 324. ν in cm^{-1} (KBr) : 2800-2000 (acidic hydrogen) ; 1600 and 1540 (C=C and C=N).

The physical characteristics of the different compounds prepared are given in Table 1.

Biological assay : All these mercapto compounds were tested against Sarcoma-180 in strain A mice. *In vitro* testings in KB cells and *in vivo* in lymphoid leukemia L1210 were carried out at National Cancer Institute, USA. None of the compounds, however, showed antitumour activity.

In vitro tests in KB cells showed ED_{50} to be 1 0×10[8] μg/ml for all the compounds, the criteria of activity being $ED_{50} \leq 6$ μg/ml *In vivo* tests against Lymphoid Leukemia L1210 were carried out in BDF_1 mice at 5 different dose levels viz., 400,

TABLE—1

Compound	m.p °C	Yield %	Formula	Analytical (%) Calcd. C	H	N	Found C	H	N	UV Absorption spectra λ_{max} in nm
I, R=$C_{11}H_{23}$	265-66	72	$C_{16}H_{30}N_4S$	62.74	8.60	18.80	62.40	8.44	17.99	324
II, R=$C_{12}H_{25}$	264-65	69	$C_{17}H_{32}N_4S$	63.75	8 75	17 50	63.90	8.59	17.12	324
III, R=$C_{14}H_{29}$	266-67	75	$C_{19}H_{36}N_4S$	65.50	9.19	16.09	65.92	9 27	15.86	328
IV, R=$C_{16}H_{33}$	263-65	76	$C_{21}H_{40}N_4S$	67 02	9 60	14.90	66.75	9.65	14.78	325
V, R=$C_{18}H_{37}$	261-64	74	$C_{23}H_{40}N_4S$	68.31	9.90	13.86	68 40	9.69	13.68	323

200, 100, 50 and 12.5 mg/kg body weight and maximum survivality was shown by V at 400 mg dose level, the T/C was 114% whereas T/C ≮ 125% was considered active[6]

Acknowledgement

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Chemical Investigation of the Stem Bark of *Canthium dicoccum*

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THE isolation of α-amyrin and oleanolic acid[1] and a new triterpene acid called canthic acid[2] from the stem bark of *C. dicoccum* Gaertn. Merr. (Syn. *C. didymum* Gaertn.) was reported earlier. The present communication reports the isolation of two coumarins, aesculetin dimethyl ether and scopoletin, and a triterpene acid sapogenin, acetyl ursolic acid from the same source.

The ethanolic extract of air-dried powdered defatted stem bark of *C. dicoccum* was concentrated and excess of diethyl ether was added to precipitate the crude glycosides The ether layer was decanted off. Two compounds, compound-A and compound-B, were isolated from the ether soluble part by preparative tlc over silica gel G. The crude glycoside obtained from the ether insoluble part was hydrolysed with acid and the aglycone part was separated into acid and neutral parts The acid part on column chromatography over silica gel gave compound-C

Compound-A, $C_{11}H_{10}O_4$ (M^+206), m p 145° [λ_{max} (EtOH): 229, 251, 257, 293 and 344 nm (log ε 4.27, 3.77, 3.68, 3.75 and 4.03 respectively). ν_{max} (Nujol mull): 1720 cm^{-1} (coumarin lactone ring). ^1H NMR spectrum · (90 MHz, $CDCl_3$, δ) · 6.23 (1H, d, J=9 5 Hz, H-3), 7.58(1H, d, J=9.5 Hz, H-4), 3 90(6H, s, 2 x-OCH_3), 6.83 (1H, s) and 6.80 (1H, s) for H-5 and H-8. Mass spectrum : m/e 206, 191, 178, 163, 135 and 120] appeared to be 6,7-dimethoxy coumarin (aesculetin dimethyl ether)[3] which was finally characterised by direct comparison with an authentic sample (m.p., mixed m.p., tlc and ir spectra).

Compound-B, $C_{10}H_8O_4$ (M^+ 192), m.p. 204° [λ_{max} (EtOH) . 230, 254, 260, 298 and 346 nm (log ε 4.10, 3.65, 3.60, 3.65 and 4.07 respectively). ν_{max} (Nujol mull): 1706 cm^{-1} (coumarin lactone ring) and 3360 cm^{-1} (phenolic-OH). ^1H NMR spectrum (80 MHz, $CDCl_3$, δ) : 6.25 (1H, d, J=9.5 Hz, H-3), 7.57 (1H, d, J=9.5 Hz, H-4), 6.20 (1H, s, phenolic –OH, partially merged with the doublet centred at δ 6.25, disappeared on D_2O exchange), 3.95 (3H, s –OCH_3), 6.89 (1H, s) and 6.82 (1H, s) for H-5 and H-8. Mass spectrum : m/e 192, 177, 164, 149 and 121] appeared to be 6-methoxy, 7-hydroxy coumarin (scopoletin)[4] which was finally characterised by direct comparison with an authentic sample (m.p, mixed m p., tlc and ir spectra).

Compound-C, $C_{32}H_{50}O_4$, m p. 286-87°, formed a monomethyl ester, $C_{33}H_{52}O_4$ (M^+ 512), m p. 243-44°. It gave pink → violet colouration in Liebermann-Buchard test and a pale yellow colouration in tetranitromethane test. ^1H NMR and ^{13}C NMR spectra of compound-C and mass spectrum of its monomethyl ester indicated the compound-C to be acetyl ursolic acid[5] which was finally characterised by direct comparison with an

authentic sample (m.p., mixed m.p., tlc and ir spectra).

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Chemical Examination of Three Indigenous Plants

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Canthium didymum Roxb.[1] (Syn. *C. dicoccum* Gaertn.) (Rubiaceae) is a low branched evergreen tree distributed in many parts of India. A survey of literature revealed that no chemical work has been done on the leaf of this plant though the bark has been examined by different workers[2-5].

Air dried powdered leaves (460 g) collected from Mayurbhanj Dist., Orissa were exhaustively extracted with rectified spirit. The alcoholic extract was divided into ether soluble and ether insoluble parts Ether soluble part was separated into acid and neutral fractions by extraction with aqueous NaOH (10%). Chromatography of the acid fraction over silica gel yielded two pure compounds A and B. Compound-A (21 mg) was crystallised from $CHCl_3$-pet. ether ; m.p. 145-146°. It showed bright blue fluorescence in uv light and gave positive test for coumarin. UV (EtOH) : 227, 251, 296, 346 ; ir : 1710, 1600 cm^{-1}. It was identified as aesculetin dimethyl ether by comparison with an authentic sample (m. m. p., tlc, superimposable ir).

Compound-B was crystallised from $CHCl_3$-pet. ether, (6 mg) ; m. p. 203-204°. It responded to colour test for coumarin and showed blue fluorescence in uv light. UV (EtOH) : 229, 252, 299, 344. It was identified as scopoletin by comparison with authentic compound (m. m. p., tlc).

The neutral fraction was chromatographed over alumina Pet. ether-benzene (7 3) eluted fraction (40 mg) furnished fine needles (ethanol) ; m. p. 209-10° $[\alpha]_D+21$ ($CHCl_3$). The compound gave positive Liebermann-Buchard test and TNM colour reaction for an unsaturated triterpene It exhibited no characteristic uv absorption above 220 nm and showed ir peaks at 3600, 1368, 1365, 875 cm^{-1}. It gave an acetate (Ac_2O-py, 100°) crystallised in needles ($CHCl_3$-pet. ether) ; m. p. 216-217°, $[\alpha]_D+48$ ($CHCl_3$). It was identified as lupeol by comparison with authentic specimen (m. m. p., tlc, ir).

The pet. ether-benzene (1 9) eluates afforded fine flakes (19 mg) ; m. p. 136-137° It gave pink-violet-blue-green colour with L-B reagent and yielded an acetate (Ac_2O-py, 100°), m p 127-128°, identical (m. m. p., tlc, ir) with an authentic specimen of β-sitosteryl acetate

Pithecellobium saman Benth. (Syn. *Samanea saman* Merill.) (Mimosaceae) is a large tree popularly known as raintree The bark and leaves of this plant have been examined chemically[6-9]. The pods were reported[10-12] to contain lupeol, α-spinasterol, α-spinasterol-β-D-glucoside, palmitic acid, stearic acid, acacic acid and mixtures of flavonoids. Our re-investigation of the pods resulted in the isolation of echinocystic acid and acacic acid lactone not reported earlier along with lupeol and α-spinasterol.

The air-dried powdered pods (618 g) of *P. saman* collected locally was soxhleted with alcohol for 62 hr. The ether insoluble part of this alcoholic extract was hydrolysed with 3% alcoholic H_2SO_4 and worked up in the usual manner. The sapogenins thus obtained were separated into acid and neutral fractions.

The neutral part, on repeated chromatography over alumina, yielded acacic acid lactone (20 mg) crystallised from ethanol as needles ; m.p. 253-255°, ir. 3400, 1760, 1371, 970 cm^{-1}. It gave an acetate (Ac_2O-py, 100°) crystallised as colourless small needles ; m p. 233-235°. The identity of the compound was established by direct comparison with authentic specimen (m. m. p., tlc, ir). The acid fraction was esterified and chromatographed over alumina. Benzene-$CHCl_3$ (1 : 1) eluted a pure compound crystallised from ethanol ; m. p. 210-211°, ir 3500, 1700, 1370 cm^{-1}. It afforded an acetate (Ac_2O-py, 100°) ; m. p. 200-203°. Finally, the methyl ester and its acetate was identified as methyl echinocystate and diacetate methyl echinocystate by comparison with authentic specimen (m. m. p., tlc, ir).

The ether soluble part, on chromatography over alumina, yielded lupeol ; m.p. 209-210° ; ir : 3400, 1639, 882 cm^{-1}, acetate m.p. 211-212°, identified as

lupeol by direct comparison with authentic compound (m. m. p., tlc, ir); ∝-spinasterol; m. p. 164-166°, acetate m. p. 179-180°, the identity was confirmed through m. m. p., tlc and superimposable ir with an authentic material.

Solanum nigrum L. (Solanaceae) is a commonly occurring hervaceous weed. The tetraploid variety of this species bears orange coloured fruits. Presence of carotenoid in these fruits was reported earlier[14]. We have characterised the fruit carotenoid as ∝-carotene.

Fresh orange coloured berries (50 g) of *S. nigrum* collected locally were ground into a paste with sand and extracted with alcohol at room temperature. The alcoholic extract was shaken with pet. ether several times. The combined pet. ether portions was diluted with ether and to this 30% methanolic KOH was added and kept at room temp in a dark place for 17 hr. The ether layer separated, washed, dried and slowly concentrated. The reddish yellow coloured residue obtained responded to colour reaction for carotenoid. It gave a single spot on thin layer chromatogram. Absorption spectra of material isolated quickly from chromatoplates were recorded in three different solvents, *n*-hexane: 421, 444, 473; CS_2. 475, 510; $CHCl_3$. 454, 484. It was identified as ∝-carotene by comparison of the spectral data with that reported for ∝-carotene[15].

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Biologically Active New 1-Substituted-2-mercaptobenzoyl-4-phenylimidazoles

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A number of compounds having various substituents at 1, 2 and 5 positions of imidazole ring have been synthesised and tested for various therapeutic effects[1-3]. 1-Aryl substitution in imidazole nucleus[4,5] enhances the microbial activity. The divalent sulphur containing molecules such as 'NCS' have also been found to possess good antimicrobial properties[6,7]. Recently, 1-aryl-2-mercaptobenzoyl imidazoles[8] were found to have good amoebicidal and fungicidal properties.

Considering the above facts, we have synthesised some new 1-substituted-2-mercaptobenzoyl-4-phenyl imidazoles and screened them for amoebicidal and fungicidal activity *in vitro*.

Experimental

Synthesis of 1-substituted-2-mercaptobenzoyl-4-phenylimidazole. Equimolecular quantities of 1-substituted-2-mercapto-4-phenylimidazole[9] and benzoyl chloride and sodium carbonate (0.015 mole) in DMF were refluxed on a steam bath for 2 hr. Later on, the reaction mixture was worked up to get a solid 1-substituted-2-mercaptobenzoyl-4-phenylimidazole. The compounds thus prepared were characterised by elemental analysis and ir spectroscopy. The following characteristic frequencies were obtained for them:

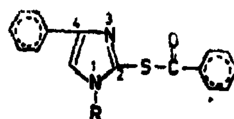
IR KBr: ν_{max} (cm^{-1}): 1660 (C=O, C_6H_5-COSR type), 1600 (C=N), 1590, 1490, 1460, 1440 (characteristic for five membered heteroaromatics), 1010-1240 (CH in-plane) and 600, 700 (CH out-of-plane).

Pharmacological screening:

Determination of amoebicidal activity[10] against Schizopyrenus russelli in vitro: The amoebae, *S. russelli*, were grown in monobacterial culture of non-nutrient agar plates (2.5% w/v agar; 0.5% w/v NaCl, *p*H 6.8-7.0) supplied with a young culture of *Eschericia coli* (2-3 days old grown on nutrient agar slages as food). A dash of fresh *E. coli* was added to freshly harvested amoebae (in 5% saline) to keep

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TABLE 1—CHARACTERISTICS AND AMOEBICIDAL ACTIVITY OF 1-SUBSTITUTED-2-MERCAPTOBENZOYL-4-PHENYLIMIDAZOLES



Sl. No.	R	m.p. °C	Yield %	Calcd. %C	Calcd. %H	Found %C	Found %H	Amoebicidal activity at the minimum inhibitory concentration of 1000 μg/ml	500 μg/ml
1.	p-$CH_3-C_6H_4$	101	51	74.5	4.8	75.0	5.7	–	–
2.	α-naphthyl	134	75	76.8	4.8	74.9	4.1	–	+
3.	o-$H_3CO-C_6H_4$	75	57	69.0	4.0	70.0	4.0	–	±
4	p-$H_3CO-C_6H_4$	66	59	69.0	4.0	70.5	4.2	–	+
5.	p-$HO-C_6H_4$	110	51	70.9	4.4	70.0	4.3	–	–
6.	o-$HO-C_6H_4$	44	51	70.9	4.4	70.9	4.1	–	+
7.	m-$HO-C_6H_4$	174	62	70.9	4.4	70.3	4.5	+	+
8.	o-$NO_2-C_6H_4$	92	61	65.8	3.7	66.0	3.9	+	+

(–)=Negative culture, (+)=Positive culture; (±)=Living and dead amoeba.

the amoebae motile and stretched. One drop of this suspension was taken in the cavity of a cavity slide and double the amount of drug concentrate (aqueous solution) to be tested (to compensate for the dilution) was added to it. Slides were incubated in moist chamber at 25±1° and observed for judging the viability of the amoebae (Table 1).

Determination of fungicidal activity[11] *in vitro* · Four species of fungi—*Aspergillus terreus*, *Aspergillus nidulans*, *Candida albicans* and *Cladosporium herbarium* were used in the present study.

Sadbouard's broth (Peptone 10.0 g/litre, dextrose 20.0 g/litre, pH 6.0 approx.) was used as the test medium. The compounds were dissolved in alcohol and 1.0 ml of test solution (100 μg/ml) was added to each tube containing an equal amount of the medium. Tubes were autoclaved at 15 lbs for 15 min prior to inoculation with suitable species of fungus. After inoculation, tubes were incubated at 26±2° for 7 days and vegetative growth recorded visually in each case (Table 2).

TABLE 2—ANTIFUNGAL SCREENING OF 1-SUBSTITUTED-2-MERCAPTOBENZOYL-4-PHENYLIMIDAZOLES

Compound No.	*A. terreus*	*A. nidulans*	*C. albicans*	*C. herbarum*
Control	++++	++++	++++	++++
1.	++	+±	+	–
2.	++	+++	+++	++++
3.	–	–	±	+
4.	–	–	+	±
5.	+	+	++	+
6.	++++	++++	++±	+++
7.	–	+	+	–
8.	++	++	++±	–+±

++ to ++++=Good growth, positive utilisation and no fungal activity.
± to ++ =Slight growth, slight fungicidal activity.
– =No growth, fungicidal activity.

Results and Discussion

All the synthesised compounds were tested for amoebicidal and fungicidal activities *in vitro*.

Compounds No. 1,2,3,4,5 and 6 show amoebicidal activity at 1 : 1000 dilution whereas compounds 1 and 5 show good amoebicidal activity at 1 : 500 dilution. Compound No. 3 show slight amoebicidal activity (Table 1)

Compounds No. 3, 4 and 7 show good fungicidal activity. Compounds No. 1, 2 and 8 show slight fungicidal activity (Table 2).

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Spectrophotometric Study of the Complexation Reaction between Oxovanadium(IV) and Gallacetophenoneoxime

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GALLACETOPHENONEOXIME (2,3,4-trihydroxy acetophenoneoxime) was earlier employed as an analytical reagent for the gravimetric[1], amperometric[2] and spectrophotometric[3] determination of various metal ions. Further study on the oxime shows that it forms a stable green complex with oxovanadium(IV) and a detailed spectrophotometric study is carried out. The solid complex is also isolated and its ir and esr spectra are studied.

Experimental

Gallacetophenoneoxime is prepared following literature procedure[4,5] and a 0.1 *M* solution of oxime is prepared in 50% aqueous alcohol.

A stock solution of vanadium sulphate (BDH, England) is prepared in double distilled water and standardised against standard potassium permanganate solution.

The instruments used for optical and *p*H measurements are the same as those reported in the earlier communication[3].

Results and Discussion

The absorption spectrum of the green complex of oxovanadium(IV)-gallacetophenoneoximate shows λ_{max} at 395 nm and broad shoulder at 560-570 nm (Fig. 1). The reagent has a little absorbance at this wavelength.

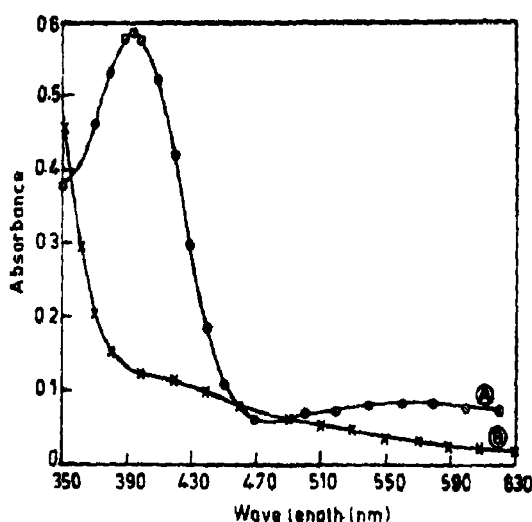


Fig. 1. Absorption spectrum of V(IV)-Oxime complex at *p*H : 4.5
(A) V(IV)-Oxime complex vs reagent blank $[V(IV)] = 5 \times 10^{-5}$ *M*.
(B) Reagent blank vs solvent mixture $[Oxime] = 1 \times 10^{-5}$ *M*.

The colour of the complex was stable within the *p*H range of 3.0-5.0 both in the buffered and unbuffered solutions. Hence all the measurements were carried at *p*H 4.5 using phthalate buffer. The absorbance of the complex remains constant for more than 24 hr. The system obeys Beer's law up to a concentration of 2.5 ppm. The optimum concentration range as per Ringbom plot[6] is 0.15-2.0 ppm. The molar absorptivity of the complex was $\epsilon = 1.54 \times 10^4$ lit. mole^{-1} cm^{-1} and the photometric sensitivity[6] was 0.0033 μg cm^{-2}. The stoichiometry of the complex in solution is established as 1 : 2 by Job's method of continuous variation method and mole ratio methods. The stability constant calculated from Job's curve is found to be 1.6×10^9.

Structure of the complex : The solid complex of oxovanadium-oxime was prepared by mixing stoichiometric proportions of ligand and metal in methanol, the *p*H was adjusted to 5 and refluxed on a water bath for half an hour. The resulting solution was concentrated and the green complex was separated out by treatment with inert solvent. The separated complex was vacuum dried over anhydrous calcium chloride. The complex is insoluble in non-polar solvents but soluble in methanol, MIBK, nitrobenzene etc.

The complex was analysed for its nitrogen and vanadium contents to determine its composition. The composition of the complex corresponds to the formula $VO(C_8H_8O_4N)_2$ in which vanadium to ligand ratio is 1 : 2. Found : N, 6.37; V, 11.61. Calcd. : N, 6.50, V : 11.82%.

The molecular weight of the complex has been determined in nitrobenzene by cryoscopic method and shows the compound to be monomeric.

A comparison of ir spectra of the complex with that of the reagent shows that the hydroxyl group frequency gets shifted from 3360 cm^{-1} in the complex. This shift in frequency is indicative of chelation to the metal. Similarly, the shifting of strong band at 1620 cm^{-1} ($\nu C=N$) in the reagent to downfield 1565 cm^{-1} in the complex is due to coordination through nitrogen of the oxime group.

The peak due to $\nu N-O$ observed at 960 cm^{-1} in free ligand is shifted to 950 cm^{-1} in the complex. The bands appearing at 990 cm^{-1} and 1125 cm^{-1} are due to V=O stretching mode. Similar observations were reported in the study of oxovanadium complexes[7,8,9].

The esr spectrum of the complex was recorded at room temperature. The $g_\parallel$ and $g_\perp$ values calculated from graph are 2.08 and 2.03 respectively.

Kivelson and Neiman[10] have shown that $g_{\parallel}$ is a moderately sensitive function for indicating covalency. Normally $g_{\parallel}$ is 2.3 or more for ionic environment and it is less than 2.3 for covalent environments. The present result shows that $g_{\parallel}$ is less than 2.3, suggesting that the complex is covalent in nature. Similar observations were also made with other ($S=\frac{1}{2}$) copper complexes[11]

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Hydrogen Ion Equilibria on *p*-Toluenesulphonylated Casein

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THE role of surface active agents in affecting changes in the biological systems is well recognised. They exert disruptive influence on the cell membrane[1], act as tuberculostatic agents[2], increase the concentration of sulphones on the cell surface, form complexes with proteins[3,4] (albumin-sodium alkyl sulphate complexes). Sulphonylated proteins are also known for their physiological activity.

In view of the above it was envisaged that modified proteins can serve as good models to understand the nature of such reactions. As a first step, investigation to determine their reaction sites is necessary It was best achieved by carrying out hydrogen ion equilibria studies by various workers particularly Linderstrom[5]. Tanford[6]. Cannon[7], Malik[8-10].

This paper gives the result of hydrogen equilibria studies on *p*-toluene sulphonylated casein along with those on the binding of H^+ and OH^- ions to whole casein reported earlier[11]

Experimental

Solution *p*-Toluene sulphonylated casein used was prepared by the method of Gurin and Clarke[12] Sulphur content was found to be 1 945% Solution of *p*-toluene sulphonylated casein was prepared at *p*H 6 5, using KOH Its concentration was determined by drying a known aliquot at 105° The correction for potassium ions was applied to get the absolute weight of protein Carbonate free hydroxide was prepared as recommended by Kolthoff[13] Potassium chloride, potassium hydrogen phthalate and sodium borate solutions were prepared by dissolving A R samples in doubly distilled water

Apparatus and techniques *p*H measurements were made on Beckmann model G *p*H meter, using glass electrodes. The *p*H meter was standardised by measuring the *p*H of 0.05 *M* potassium hydrogen phthalate for the acid range and that of 0 01 *M* sodium borate for the alkali range Purified nitrogen was passed slowly for about 10 min to ensure inert atmosphere

Optical density was measured with Unicam spectrophotometer type SP 500, using a hydrogen lamp (slit width 0 1 mm and silica cells of 1 cm path).

Procedure. Varying amount of hydrochloric acid (0 0861 *M*), viz 2.0, 1.6, 1.0, 0.8, 0.5, 0.3, 0.1 and 0.02 ml and 0.2, 0.4, 0.6, 0.8, 1.0, 1.1, 1.2 and 1.5 ml of potassium hydroxide (0.0605 *M*) were taken in different pyrex tubes. Two such sets were prepared. In one set, protein was not added and total volume was made upto 10.0 ml by adding 1.5 ml of 1 0 *M* potassium chloride (to maintain constant ionic strength) and water. In the second set, the total volume was made 10 ml, by adding 4 ml of *p*-toluene sulphonylated casein solution (2 0%) and 1.5 ml of 1 0 *M* potassium chloride solution and water The *p*H values of these solutions were then recorded at two different temperatures, viz, 20° and 30° The results are reported in Tables 1 and 2.

Experiments were also performed to show the reversible nature of hydrogen ion equilibria of the protein both in the acidic and basic range[14] of *p*H. The hydrogen ion titration curve was found to be reversible at moderate *p*H values.

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TABLE 1—HYDROGEN ION BINDING DATA ON p-T. S. CASEIN AT 20°

Ionic strength =0.15
Total volume =10 ml
Protein concentration =8.0 g/litre

H⁺ added (moles/litre × 10⁻⁸)	pH_1 (without protein)	pH_2 (with protein)	Bound H⁺ mole /10⁵ g of protein	Moles H⁺ dissociated per 10⁵ g of protein
17.22	1 9	2.2	108	33
13.78	2.1	2.4	108	38
8.61	2 25	3.5	92	49
6.89	2 85	4.0	84	57
4.31	2.45	4.9	54	87
2.58	2 65	5.3	32	109
0.86	3.1	5.7	11	130
0.17	3.70	6.0	2	139
OH⁻ added (moles/litre 10⁻⁸)				
1.21	10.1	7.0	15	156
2.42	10.2	7.55	30	171
3 68	10.9	8.8	44	185
4 84	11 0	9.05	59	200
6.05	11.25	9.55	75	216
6.65	11.25	10.35	75	216
7.26	11.5	10 75	75	216
9.08	11.9	11.0	99	240

Fig. 1, Curve (a)

TABLE 2*—HYDROGEN ION BINDING DATA ON p-T. S. CASEIN AT 30°

Ionic strength =0 15
Total volume =10 ml
Protein concentration =8 0 g/litre

H⁺ added (moles/litre × 10⁻⁸)	pH_1 (without protein)	pH_2 (with protein)	Bound H⁺ moles/10⁵ g of protein	Moles H⁺ dissociated per 10⁵ g of protein
0.17	3.60	5.85	2	139
OH⁻ added (moles/litre × 10⁻⁸)				
1 21	9.40	6.90	15	156
2.42	10 10	7.40	30	171
3.63	10 25	8 60	44	185
4.84	10.90	8 80	60	201
6.05	11.00	9.25	75	216
6.65	11 05	10 05	75	218
7 76	11.20	10.45	75	216
9.03	11.55	10 75	98	239

* Data below pH 6.0 are the same as at 20° hence not included.

Fig 1, Curve (b)

To determine the ratio of tyrosine and tryptophan groups of the protein, it was dissolved in 0 1 N KOH and optical densities were measured at 281 and 294 nm. The results are given in Table 3.

Calculations : The bound hydrogen and hydroxyl ions were determined by the following relationships[6,7].

TABLE 3—PROTEIN CONCENTRATION=8 0 g/litre
IONIC STRENGTH=0.15
TEMPERATURE=20° AND 30°

pH_1 at 20°	pH_2 at 30°	Moles of H⁺ dissociated per 10⁵ g of protein	$\Delta H_{ion} \times 10^3$
4.0	3.95	57	1.9865
4.90	4.85	87	1.9865
5 30	5.25	109	1.9865
5.70	5.65	130	1.9865
6 00	5.95	139	1.9865
7.00	6.90	156	3 8700
7.55	7.40	171	5 8000
8 80	8 60	185	7.7460
9 05	8 80	200	9.6800
10.25	10 05	216	11.6100
10.75	10 45	216	11.6100
11.05	10.70	240	13 5500

Fig. 2

$$(C_1 - C_2)/g = C_1/g[1\text{-antilog}\,(pH_1 - pH_2)]$$

for bound hydrogen ions and

$$(C_1 - C_2)/g = C_1/g\,[1\text{-antilog}(pH_2 - pH_1)]$$

for bound hydroxyl ions, where g is weight of the protein in gm, C_1 and C_2 are the concentration in gm moles/litre of the acid with and without the protein and pH_1 and pH_2 are the corresponding pH values. The results are given in Tables 1 and 2.

The apparent heat of ionisation (ΔH_{ion}) was determined according to Wyman's[15] method using the equation :

$$\Delta H_{ion} = -2.303RT^2\left(\frac{dpH}{dt}\right)_\gamma$$

where dpH is the change in pH with change in temperature dt at a fixed value of γ (the number of hydrogen ion dissociated per 10^5 g of protein).

The ratio of tyrosine and tryptophan groups was calculated by the method of Beaven and Holiday[16] using the following formula :

$$\frac{M_{Tyrosine}}{M_{Tryptophan}} = \frac{0.592\,E_{294} - 0.263\,E_{280}}{0.263\,E_{280} - 0.170\,E_{294}}$$

where E_{280} and E_{294} are the extinction coefficients of the protein in 0.1 N KOH at 280 nm and 294 nm.

As the exact molecular weight of p-toluene sulphonylated casein is not known, all the calculations have been made for 10^5 g of the protein.

Results and Discussion

The results on hydrogen ion equilibria studies of p-toluene sulphonylated casein, worked out at two different temperatures, viz. 20° and 30°, provide valuable information regarding the different ionisable groups present in the protein. The whole titration curve may be divided into three different portions by the method of Cannon[17], each region corresponding to a set of intrinsically identical groups :

(i) The first region is attributed to the ionisation of those side chain carboxyl groups not present as amides (α-carboxyl at the end of peptide chain

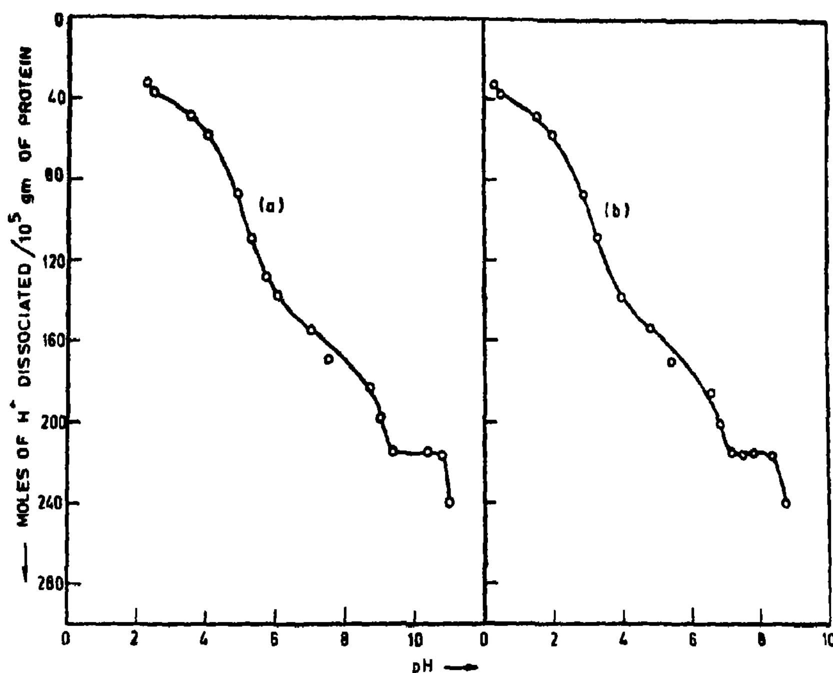


Fig. 1. Titration curves of *p*-toluene sulphonylated casein.

and β-carboxyl group from aspartyl and glutamyl residues of the protein).

(ii) The second region is attributed to the imidazole groups from the histidine residue.

(iii) The third region is not always defined and is due to α-amino (at the end of the peptide chain), ε-amino groups of lysine, phenolic hydroxyl groups of tyrosine residues, guanidinium groups of arginine residues.

The titration curves at high and low *p*H values permit an estimation of the maximum base and acid combining capacity of *p*-toluene sulphonylated casein. In addition to the usual ionising groups found in most proteins, the *p*-toluene sulphonylated casein contains amount of phosphoric acid just like whole casein that must be considered in an analysis for the anionic groups. According to Cannon *et al*[17] a phosphate group in egg albumin may be expected to contribute two equivalents to the titration curve, one in the carboxyl region at about *p*H 2 and the other in the imidazole region at about *p*H 7.0. It is not easy to establish from these curves definite transition points representing the ionisation of specific groups. *p*H values of 6.35 and 9.30 have been selected since these values give the results from α-, β- and γ-casein[18] and agree with the analytical data of Gordan *et al*[11]. They are also consistent with the values given by Scatchard[19] for the binding of hydrogen ions for the various types of groups in other proteins under similar condition. At *p*H 6.35, the titration curves give the number of carboxyl groups plus one equivalent of phosphoric acid and at *p*H 9.3 give the number of carboxyl groups plus imidazole groups and two equivalent of phosphoric acid. Based on the *p*H values, the calculated values for the ionising groups for α-, β- and γ-casein are in agreement with analytical results for α-, β- and γ-casein[18].

The carboxyl region: The upper portion of titration curve of *p*-toluene sulphonylated casein obtained at 20° [Fig 1, curve (a)] represents the dissociation of hydrogen ion from phosphoric acid and the carboxyl group of *p*-toluene sulphonylated casein and hence may be used to determine the number of these groups. It is clear from Fig. 1, curve (a) that at *p*H about 6.35, the curve starts flattening, indicating complete ionisation of the carboxyl and phosphate groups. The value of γ at *p*H 6.35 comes out to be 140. This value finds further support from the data of apparent heat of ionisation (Fig. 2) since sharp inflexion occurs at $\gamma = 140$ corresponding to $\Delta H_{ion} = 1.936$ Kcals/10⁵ g of protein. This value is within the expected range of carboxyl groups (Table 4)

The non-carboxyl region The expected range of ionisation of imidazole groups of protein is between *p*H 6.35 to *p*H 9.3 and hence the value of the number of hydrogen ions dissociated per 10^5 g of protein between this range may be utilised to determine the number of imidazole groups. This value comes out to be 18 at *p*H 9.3. The results on apparent heat of ionisation for these groups also support the above data since ΔH value of 6.8 Kcals/10^5 g of protein, which is the expected value for these groups, is obtained (Table 4).

The analysis of the basic portion of the curve (i.e. beyond *p*H 9.3) is difficult to explain due to overlapping of the titration regions of different

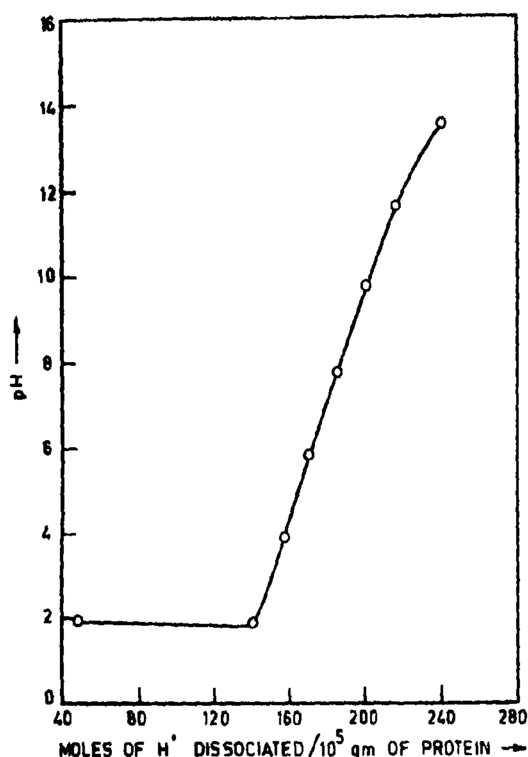


Fig. 2. Relation between apparent heat of ionization and the total no. of H^+ dissociated per 10^5 gms of protein.

TABLE 4—APPARENT HEAT OF IONISATION OF IONISING GROUPS OF *p*-TOLUENE SULPHONYLATED CASEIN

Ionisable groups	Expected range for ΔH_{ion} (Kcal)	Observed average value for ΔH ion (Kcal)
Carboxyl	±1.5-3.0	1.9365
Imidazole	7.0	6 600
Amino	10-12	—
Guanidinium	12-14	13.600

groups. However, the average value of γ between 9.3 and 10.5 (expected range for the ionisation of amino groups in proteins) may be taken as the number of total amino groups present in *p*-toluene sulphonylated casein. However, it has been found from the titration curve (Fig. 1) that no change in the number of hydrogen ions dissociated per 10^5 g of protein is observed beyond *p*H 9.3. The constancy upto *p*H 10.5 shown by the flat portion in the hydrogen ion titration curves [Fig. 1, curves (a), (b)] is due to the masking of the amino group of the protein as a result of sulphonylation. This fact has been further supported by the result of apparent heat of ionisation (Fig. 2).

Arginine is not directly estimated by titration since guanidino groups are too strong a base to be converted to the unified form in any significant amount at any *p*H (even upto 11) where accurate measurement is possible. Beyond this *p*H, the titration data do not give reliable results. The results on apparent heat of ionisation comes out to be 22, corresponding the ΔH_{ion} value of 13.55 Kcals/10^5 g of protein (Fig. 2).

Tyrosine and tryptophan groups : Since potentiometric method could not be used as such to determine the number of these groups, spectrophotometric method was employed to determine the ratio of these groups. The spectrophotometric value of 5.14 for the ratio of these groups is in close resemblance with analytical[20] value of 5.83 for these groups.

A comparison of the hydrogen ion equilibria data of *p*-toluene sulphonylated casein with that of casein is given in Table 5.

TABLE 5—IONISABLE GROUPS IN NATIVE CASEIN AND *p*-TOLUENE SULPHONYLATED CASEIN

Groups	Reasonable* analytical values in Casein/10^5 g	Observed in case of *p*-T.S. Casein/10^5 g	Observed in case of *p*-T.S. Gelatin/10^5 g
α-Carboxyl β-Carboxyl	96	94.0	110
Imidazole	20	18.00	4
Amino	56	—	—
Guanidinium	28.5	22	42
Tyrosine/Tryp.	5.83	5.14	—
Total Cationic	100	40	46

* Reference 11.

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Determination of Sodium Carboxylates by Reaction with ω-Bromoacetophenone

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CARBOXYLATES can be acidimetrically titrated with hydrochloric and perchloric acids[1], using either visual or potentiometric indication. The silver salt method[2] does not hold reliability, primarily due to the sensitivity of the silver salts towards light and air and secondly due to the non-stoichiometric composition of the salts obtained from the aromatic acids containing two nitro groups. The combustion approach[3] for determining metal carboxylates involving the oxidation of the sample to the corresponding carbonate followed by determination of the latter is quite time consuming.

A titrimetric procedure for the determination of carboxylates based on quantitative reaction with ω-bromoacetophenone, has been developed. A sodium carboxylate is reacted with ω-bromoacetophenone in acetonitrile-water medium, the excess of the latter being determinable by reaction with thiourea resulting in the formation of 4-phenyl-2-aminothiazole hydrobromide[4], titratable[5,6] with alkali, using phenolphthalein as indicator. Though tested with a selection of sodium carboxylates, the procedure seems to hold general applicability. The accuracy of the procedure is evident from the standard deviations of the results. The procedure, therefore, merits recommendation.

Experimental

A weighed quantity (0.2-1.0 mmole) of a sodium carboxylate and ω-bromoacetophenone, in two-fold excess, are dissolved in 12 ml of acetonitrile-water (10 : 2). The solution is refluxed for the required period of time as recorded in Table 1 followed by the addition of excess of thiourea at room temperature (25°). The solution is allowed to stand for 10 min and 4-phenyl-2-aminothiazole hydrobromide, thus formed, is titrated against 0.1 *M* sodium hydroxide, using phenolphthalein (3 drops, 0.5% solution in ethanol) as indicator to a light pink colouration holding stability for a min.

TABLE 1—DETERMINATION OF SODIUM CARBOXYLATES

Carboxylate*	Recovery Average %	Reaction period (min)	Standard deviation
Acetate (4)	99 83	30	0 08
n-Propionate (3)	100.00	45	0 02
n-Butyrate (4)	99 98	45	0.06
Benzoate (4)	99 95	30	0.08
o-Chlorobenzoate (4)	99.99	30	0 08
p-Chlorobenzoate (4)	99.92	30	0 08
p-Aminobenzoate (3)	99.77	45	0.28
3,5-Dinitrobenzoate (4)	99 96	30	0 06
Phenylacetate (4)	99.91	30	0 07
Phenoxyacetate (4)	99 81	30	0 17

* Figures in parentheses represent number of determinations.

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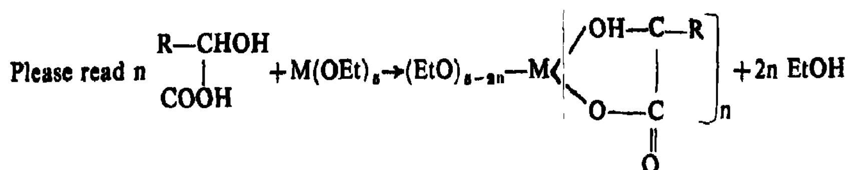
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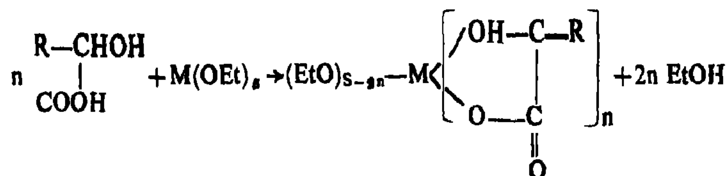
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Page 195, 1st column, equation at the bottom



for



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Effects of P and Fe Concentrations in the Medium on the Uptake and Distribution of Fe in Maize Plants (*Zea Mays* L.)

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The subject of the study is the influence of P and Fe concentrations in a nutrient solution on the translocation of Fe With high P concentrations in the nutrient solution, Fe translocation is affected at all Fe levels, while with high Fe concentrations translocation is also affected when P concentrations are low.

IN many cases, an inadequate amount of Fe is the result of Fe acting on other nutrients and *vice versa*. P is one of the macro-nutrients that take part in this interaction.

The phosphate ion may affect Fe nutrition either through a precipitate mechanism before it is absorbed by the plants[1] or through an inactivating process within the plant[2,3].

The present study concerns the effect of P and Fe concentrations in the nutrient solution.

Experimental

For the indoor experiment, a hybrid maize (*Zea Mays* L., H 209) was cultivated hydroponically. "Absorption through the air" was the method used, which is the same as Van Dried's.

The nutrient solution contained varying P and Fe concentrations, while the remaining nutrients remained unchanged[4].

The experiment factorially combined 4 P levels (1, 10, 100 and 1000 μM) with 3 Fe levels (10, 20 and 40 μM).

The plants were analysed in their phenological state corresponding to pollination and the amount of Fe in the root, stalks and leaves was established through spectrophotometry on the principle of atomic absorption.

Results and Discussion

The Fe concentration in the roots (Fig. 1) shows a tendency towards minimal Fe absorption in more developed plants This was already observed in barley[5]. It is as if highest yield was coupled with greater Fe mobility or a lesser need for this element However, other plants, such as beans, act differently, i.e. the Fe concentration is higher in the roots that are more developed[6].

While there is a tendency towards a lower Fe concentration in the root, it was also observed at the same time that the P concentration in the nutrient solution increased to maximum yield (100 μM P)[7].

With the same P level in the nutrient solution, the Fe concentration in the root shows a tendency

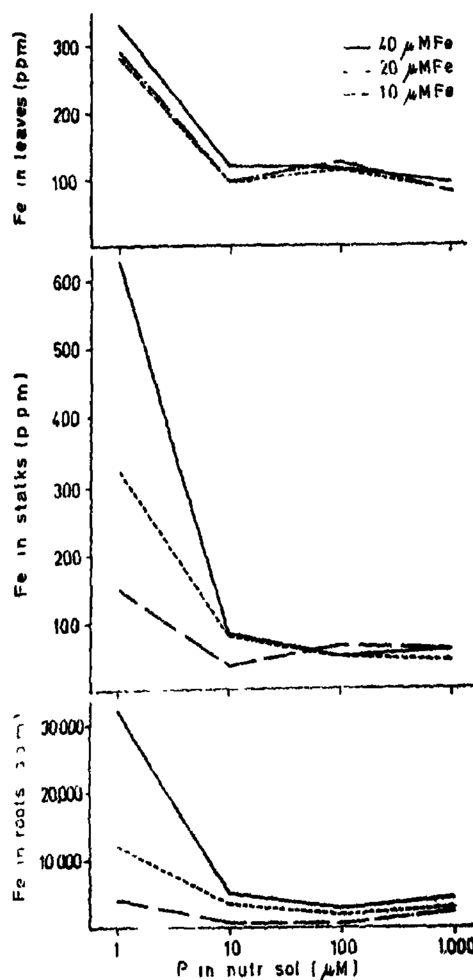


Fig. 1. Effect of P and Fe concentrations in the nutritive solutions on the Fe levels in the roots, stalks and leaves of maize plants.

to increase when the Fe level in the solution is increased. This is logical and occurs with all P levels that were studied.

What happens in the root also happens in the stalks except that the amount of Fe in the stalks does not increase with the Fe concentration in the nutrient solution for adequate or higher P concentrations (100 and 1000 μM).

With regard to the leaves, the observations made with the root and stalks do not apply. It appears as if Fe in the leaves act more independently compared to the Fe in the nutrient solution.

With the highest Fe level (40 μM), Fe concentration in the leaves decreases when the P concentration in the nutrient solution is increased, the same as in the root and stalks. However, in the leaves, this process continues even after reaching the best yield levels. We believe that translocation in the leaves is more important than absorption as such. This explains the general tendency for Fe to decrease while P increases in the solution, the latter making mobility more difficult for the former.

The effect of a decreased Fe concentration in the leaves after an increase of the P level in the nutrient solution was observed in blueberry plants[8].

A bibliographic survey of the subject shows, however, that hybrid maize plants Y_{S1}/Y_{S1} which were treated with a nutrient substance containing a high level of P presented lower Fe concentrations in the root when the P concentration in the nutrient solution was increased. This appears contradictory, at first, to what we observed. A lower Fe concentration is observed in the part of the plant that remains surrounded by air, an observation that coincides with ours. The apparent contradiction, referred to above, may be the result of a saline effect in the nutrient solution since the Fe concentration with which the maize plants are treated (100 μM Fe) is higher than the one used by us (10, 20 and 40 μM Fe)[9].

The relation $[Fe_{in\ tops}]\ /\ [Fe_{in\ roots}]$ (Fig. 2) shows that there are no differences in the lower Fe level (10 μM) in plants treated with a nutrient solution where the P concentration was between 1 and 100 μM. However, a decrease is observed with high P concentrations (1000 μM) and the ratio for normal and higher Fe levels (20 and 40 μM) is optimal with a P concentration of 100 μM, while a decrease occurs both with higher and lower concentrations. This leads to the fact that for low Fe concentrations, Fe translocation suffers mainly with high P concentrations, while with high and normal Fe concentrations in the nutrient solution translocation suffers both with high and low P concentrations. This confirms the existence of an optimal P/Fe ratio, especially with regard to Fe mobility in the plant.

With high P levels in the nutrient solution, maize plants develop symptoms of chlorosis. This may be due to an increasing amount of P in the tissue which produces a greater amount of Fe combined with phosphate. As a result, there is a smaller amount of Fe that can be assimilated

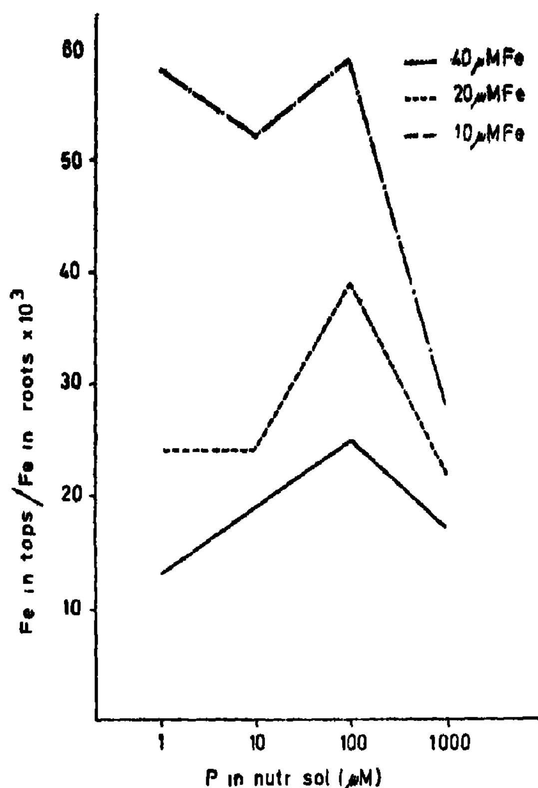


Fig. 2. Relationships between Fe_{tops}/Fe_{roots} and P in nutrient solutions for each level of Fe in the medium.

through the functions of the nutrient inside the plant, such as the chlorophyll-producing function[9]. Since the Fe combined with phosphore-proteins in the plant cells is ferric and not ferrous, the reason for the P/Fe ratio may be a measure to ensure ferric-ferrous balance in the cells[10].

Through a study of autoradiograms, it was observed that high P concentrations in the nutrient solution made Fe absorption and translocation impossible since the plants resisted interveinal translocation, perhaps because Fe was inactivated or precipitated in the veins and translocation of mesophyll did not take place[11].

In conclusion, it may be said that Fe translocation in the maize plant depends on the P concentration in the nutrient solution when the Fe concentration in the solution is high. In all the other cases, only high P concentrations in the solution have an effect on Fe.

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Some Reflections on Ways to Bring About a Permanently Sustainable World Agriculture

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IS an ecological approach necessary to achieve a sustainable world agriculture? I believe the answer is "yes" and that this, in its turn, implies agricultural techniques based on the biological requirements of soil, plants, and animals (including Man). The aim of such techniques is *optimum* production rather than *maximum* production and entails a system of farming and gardening which is primarily "organic".

In recent years an increasing number of scientists, *and* practical cultivators, have come to share this view, but there is still a very widely held opinion in official circles that intensive chemical farming provides the only hope of feeding the expanding world population and has therefore to be accepted whether we like it or not. To me it seems probable that the exact opposite could prove to be the case, and that it is an alternative and largely organic agriculture that will be forced upon us whether we like it or not. This is because, as is becoming increasingly apparent, the days of the former are numbered. One reason is the enormous demand on the world's non-renewable resources of energy, made by our Western life-style in general and modern farming techniques in particular. Another is that modern methods are putting strains on the biota which is causing it to collapse.

Thus it is only common sense to look at alternatives, and in all seriousness study their potential viability. It is not yet, however, generally accepted that the days of our present methods and behaviour are numbered. Even where it is, it is too often regarded as a long term problem which must not be allowed to obscure the immediate objective, namely the need to increase quantitative food production now. Here it is argued that organic farming is less efficient, that it has to rely on re-cycling which is wasteful, so that, were it to be adopted, world food production would inevitably be lower, particularly production of protein at a time when what we need is to produce ever more per acre.

To this I would like to point out three things:

1. A common view among nutritionists today is that the amount of protein (especially animal protein) hitherto thought to be required by man has been greatly overestimated (organic farmers have found this also to be true for livestock).
2. There need be little loss in re-cycling if we did not waste so much.
3. Certainly we need to produce more per acre. Unfortunately the yardstick of modern economics is to measure efficiency by production per *man*.

For over half the world this yardstick makes no sense whatsoever—in rich, highly industrialised western countries it has been possible in the past (it is increasingly less so) to make out a case for replacing human labour by high capital-cost machinery Elsewhere in the world, circumstances require nearly the exact opposite. The measurement of efficiency then becomes (and will have, eventually, to apply to the "west" too) production per *unit of land*.

The key to success for this is not imported high capital-cost technology - so often excessively violent in operation, and which appears to deify giantism - but "appropriate", human scale, technology (as advocated by the late Dr. Schumacher) utilizing, as far as possible, local resources and able to cater for the needs of regional communities.

In any case labour-intensive small units, in which the T.L.C. factor can play a part (Tender Loving Care), will always be able to produce spectacularly more per acre than large mechanised farms.

When the inevitable change in western life-style takes place, I predict that we shall find it easier than now to feed the world population because western nations will presumably have become less gluttonous (and consequently probably also be healthier)!

We still hear, though less frequently than we used to, the argument that there is no scientific basis for advocating exclusive use of organic manures, such as FYM and compost, because "there is absolutely no difference between a plant nutrient contained in organic materials and the same nutrient in inorganic chemical form". There may be no chemical, or other easily analysable, difference, but as Dr. Dhar's work, among others, has clearly shown there is a demonstrable functional difference—to give one example—anything having an effect on root distribution may have an effect on plant nutrition because it will influence the volume of soil explored. Thus good soil structure in depth, such as is obtained in a biologically active soil, can improve productivity simply by increasing the depth of soil exploited for water and nutrients. There is now well documented scientific evidence that fertilizer concentrations of N and P have an influence on localised root branching[1]. They induce

it at the expense of deep rooting exploration. This could well lead to luxury uptakes of N and P linked to inadequate uptake of other nutrients. There are implications in this for nutrient unbalance in the crop and thereby some risk of nutrient unbalance in the animals and humans feeding upon it. If root activity is a factor in the development and maintenance of soil structure, there are also implications in this for the overall pattern of soil development.

In a biologically active soil, which implies one adequately provided with organic matter and natural rock minerals, the latter are released as the plant wants them, moreover the roots are presented with a complete diet from which they can pick and choose. Plants are highly selective in such circumstances, hence the value of some of the deep rooting weeds (which the organic farmer calls herbs when he sows them deliberately). Normal chemical fertilizers, apart from the disadvantage just mentioned are far too simple. A plant's mineral requirements are many times wider in range. By giving only two or three which stimulate bulk growth, others, equally important, are exhausted, or locked up in the immediate neighbourhood of the rhizosphere, thus leading, as already mentioned, to unbalanced nutrition of the plant and often, through their solubility, to serious environmental pollution.

Plant nutrients do not, as was once taught, all have to be reduced to simple inorganic solutions in order to be absorbed. Plants can ingest quite complex organic molecules, unbroken. The history of D.D.T. provides irrefutable evidence for this. So do such symbiotic mechanisms as mycorrhizal association, whereby the plant may well derive some nutrient equivalent to vitamins in animal nutrition.

A possible additional factor for which, I readily admit, there is at present no scientific proof but which seems to me to provide an interpretation consistent with many observations, is that, in nature's food-chains, a plant's normal method of mineral intake is not direct, but second-hand, the mineral plant-foods being, as it were, by-products of the activity of the soil micro-flora and other members of the soil population.

Such by-products have a far more complex and comprehensive formula than N, P and K and moreover are living substances. Inorganic chemicals are inert. A food-chain is not only a material circuit but also an energy circuit. Soil fertility has been defined as the capacity of soil to receive, store and transmit energy. A substance may be the same chemically but very different as a conductor of living energy. The hypothesis is that the energy manifesting in birth, growth, reproduction, death, decay and rebirth, can only flow through channels composed of living cells, and that when the flow is interrupted by inert matter it can be short-circuited with consequent damage to some part of the food-chain, not necessarily where the block occurred. The Anthroposophical Society's Research establishment at Dornach in Switzerland has provided some evidence which appears to support such a view.

I would like to see much more research undertaken in this field.

Now I want to put forward what I believe our aims should be in evolving a sustainable agriculture and give my own interpretation of biological husbandry. In doing the latter I recognise that any examples I give are taken from my personal experience of farming and gardening in the Northern Hemisphere, and on soils mainly of ex glacial origin but in my many travels I have seen the principle underlying the techniques I describe, successfully applied in a wide variety of climates, conditions and soils, including some of the highly vulnerable tropical soils, where modern western technology can be, and has on occasion been, disastrous. While techniques must vary according to local conditions the principle is quite simple. It consists of recognising that the soil is a complex living entity and treating it as such.

The criteria for a sustainable agriculture can be summed up in one word—permanence, which means adopting techniques that maintain soil fertility indefinitely; that utilise, as far as possible, only renewable resources; that do not grossly pollute the environment, and that foster life energy (or if preferred biological activity) within the soil and throughout the cycles of all the involved food-chains.

This is what biological husbandry sets out to attempt—with an increasing degree of understanding and success among its practitioners. Throughout the world, as a result of their own experience, these cultivators sincerely believe that they can offer a genuine and viable alternative agriculture, capable of solving many of the problems of mankind. This possibility, as well as the need for it, is becoming, as I mentioned earlier, increasingly recognised in academic and scientific circles.

As a result of this, much valuable practical research is at present going on in some European countries to adapt and improve traditional biological techniques and tools to render them better suited to present day needs, both in the west and in the Third World.

I am often asked how, in a broad sense, I define "Organic Farming" as opposed to conventional farming. Though I prefer the term "biological husbandry" because of its emphasis on life, the short answer is *Balance*; however, I think it is necessary to amplify a little.

Contrary to the views held by some, I am sure that the techniques of "organic farming" cannot be imprisoned in a rigid set of rules. They depend essentially on the outlook of the farmer. Without a positive and ecological approach it is not possible to farm organically. The approach of the modern conventional farmer is negative, narrow and fragmentary, and consequently produces imbalance. His attitude to "pests" and "weeds", for example, is to regard them as enemies to be killed—if possible exterminated. When he attacks them with lethal chemicals he seldom gives a thought to the effect this may have on the food supply or habitat of

other forms of wildlife among whom he has many more friends than foes. The predatory insects and the insectivorous birds are obvious examples.

The attitude of the organic farmer, who has trained himself to think ecologically, is different. He tries to see the living world as a whole. He regards so-called pests and weeds as part of the natural pattern of the biota, probably necessary to its stability and permanence, to be utilized rather than attacked. Throughout his operations he endeavours to achieve his objective by co-operating with natural agencies in place of relying on man-made substitutes. He studies what appear to be nature's rules—as manifested in a healthy wilderness—and attempts to adapt them to his own farm needs, instead of flouting them. One of the first things he will notice about a natural eco-system, such as a wilderness or a natural forest, is balance and stability. The innumerable different species of fauna and flora that go to make up such a community, achieve, as a result of their interdependence, whether in co-operation or competition, collective immortality. Seldom, if ever, is any species eliminated ; seldom, if ever, does any species multiply to pest proportions.

Thus the organic farmer, if he has a crop badly attacked by some pest, let us say, (and this can happen, even to organic farmers !) recognises that this is a symptom of imbalance in his local environment, and he first looks to see if some faulty technique of his own has been responsible—often it has. This does not mean that he can always avoid emergency remedial measures but these he employs only when there is a real emergency, not as a routine. He strives instead to bring about biological balance, and it is remarkable the extent to which the organic farmers and growers do in fact achieve this. I could give you several examples, but one must suffice.

Some years ago a large scale organic commercial grower of my acquaintance, growing vegetables, fruit and flowers, was visited by a team of scientists from Cambridge University—they included plant pathologists and entomologists. They knew it was an unsprayed holding and they came looking for disease and pests. They found isolated examples of everything they expected to find, but, as they put it, they failed to find a single case of crop damage.

Besides biological balance, the ecologically minded organic farmer takes note of, and tries to apply, other apparent biological rules. For example nature's diversity of species he adapts through rotations, under-sowing, and avoiding monoculture of crops or animals. Nature's habit of filtering sunlight and rain through some form of protective soil cover he adapts by such practices as cover-cropping and mulching. Top soil on the top appears to be nature's plan. Organic matter is always deposited on the surface. It is left to the earthworms and some insects to take it below. The organic farmer also puts his compost and farmyard manure on, or very near, the surface, and in carrying out mechanical cultivations keeps soil-inversion to a minimum, the tine cultivator being preferred to the plough.

Nature's highly efficient re-cycling system ensures provision of living food for all organisms in the food chain from soil bacteria and fungi to large fauna ; the organic farmer therefore lays great stress on the conversion and return to the soil of all organic residues. His aim is to feed and to assist proliferation of the soil population and to leave it to feed the crop

Finally, and of equal importance, he notes, and tries to reproduce, the almost perfect structure of a biologically active soil which alone ensures the three most important characteristics of a fertile soil—good aeration, water-holding capacity, and free drainage.

It is quite astonishing the extent to which this all-important property of good soil is neglected in modern agriculture Poor soil structure leads to imbalance between water and air in the pore spaces of the soil Many apparent mineral or trace mineral deficiencies in the soil turn out to be oxygen deficiencies. When that is corrected the others disappear In most agricultural soils there is really plenty of mineral plant food for the nutritional requirements of plants, even when continuously cropped, if their roots are allowed to exploit it downwards. The key to this is good soil structure which is greatly influenced by the activity of earthworms The techniques of modern farming tend to destory good structure in a number of ways, such as by the impaction of heavy implements, by carrying out cultivations in unsuitable weather conditions, and by failure to provide sufficient organic food and/or a suitable lime status for the earthworm population (or its equivalent in tropical soils).

All these faults are the outcome of failure to think ecologically—they are symptoms of a degree of fragmentation in our approach to the living world which has become a real threat to our survival. Throughout biological evolution, starting from single celled organisms right up to the complexity of rain forests, the process has been characterised by increasing diversity among species, lengthening of the food chains, and progressive enrichment of the environment. For the first time in the history of the planet the actions of modern man appear to be putting this process into reverse. Whole species of fauna and flora are being eliminated, the food-chains are becoming shorter, and the environment progressively impoverished. It only takes a little imagination to picture what could happen if the trend continues.

What are we going to do about it ? This is the real challenge, and in my view it is one of education.

It is urgently necessary that the broadest possible aspect of ecology should form part of the regular curriculum of all schools, starting at the primary stage. The trouble is we have first to teach the teachers, and here, I think, we must be agreed on what we want to teach. There are two motivations

behind an ecological approach—one is based on self interest, however enlightened, i. e. when consideration for other species is taught solely because on that depends the survival of our own. This approach can still lead to harmful fragmentation.

The other motivation springs from a sense that the biota is a whole, of which we are a part, and that the other species which compose it and helped to create it, are entitled to existence in their own right. This is the wholeness approach and it is my belief that the survival of planet Earth depends on its wide acceptance.

If I am right, this means that we cannot escape from the ethical and spiritual values of life for they are part of wholeness. To ignore them and their implications would be to pursue another form of fragmentation.

Therefore, I hold that what we have to teach is the attitude defined by the late Aldo Leopold as "A Land Ethic". This requires that we extend the concept of Community to include all the species of life with which we share the planet. We must foster a reverence for all life, even that which we are forced to control, and we must, as Leopold put it—"Quit thinking about decent land use as solely an economic problem, but examine each question in terms of what is ethically and esthetically right, as well as what is economically expedient. A thing is right when it tends to preserve the integrity, stability and beauty of the biotic community. It is wrong when it tends otherwise".

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Integrated Nutrient Supply to Soil for Soil Productivity

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AN idea of the nutrients removed from soil by one tonne of grain of paddy and wheat and straw can be obtained from Table 1 (Bhumbla[1]).

TABLE 1—NUTRIENTS (kg) REMOVED FROM SOIL BY ONE TONNE OF GRAIN OF PADDY AND WHEAT

Crop	N	P_2O_5	K_2O
Paddy	30	12	50
Wheat	35	15	40

The main source of nitrogen in the soil is organic matter. When the soil organic matter content is high, the decomposition of the organic matter may adequately meet the nitrogen needs of the plant. However, under the climatic conditions prevailing in tropical and sub-tropical regions the amount of organic matter in the soil is quite low.

Recycling of plant nutrients would involve use of bulky organic matter and biological nitrogen fixation, along with chemical fertilizers. Currently, this has become very important because of the high fertilizer cost.

Biological nitrogen fixation: One important source of soil nitrogen is nitrogen fixation in the soil, both *symbiotic* and *non-symbiotic*.

Symbiotic nitrogen fixation: The amount of nitrogen fixed by the grain legumes is abont 60-80 kg per hectare, most of which is removed in the form of grains But in fodder legumes like berseem, the fixation may be as high as 400 kg per hectare The fodder legumes will not only improve the nutrition of the cattle but also result in increased availability of nitrogen in the dung voided by the animals[1].

Non-symbiotic nitrogen fixation: Recent work on non-symbiotic nitrogen fixation in soils growing paddy indicates that the non-symbiotic nitrogen fixation (including blue green algae) may be of the order of 50-60 kg per hectare. Data from permanent manurial experiment in India in the irrigated areas indicate that it is possible to get 1.7 to 2.0 quintals of paddy per hectare without addition of fertilizers, but for any further increase, it would be necessary to supply nutrients in the form of chemical fertilizer or manure or symbiotic nitrogen fixation[1].

Use of chemical fertilizers: The loss of nitrogen from applied nitrogenous fertilizers through leaching and through volatilisation of nitrogen will be considerable and normally the recovery of applied nitrogen is of the order of 35-60%. Losses of phosphate by leaching or by volatilisation is negligible but the recovery in a crop season may be 20-40% Continuous addition of phosphatic fertilizers does result in the build up of soil phosphorus which later becomes available to the subsequent crops. Availability of potassium under tropical and sub-tropical conditions of India has been found to depend upon the weatherability of the clay minerals and the potassium needs of the crop.

Because of high prices and shortage of chemical fertilizers the aim should be to obtain maximum return from unit fertilizers applied, rather than maximum yield per unit area The fertilizer should be applied on the basis of (i) soil test, (ii) crop variety and (iii) expected yield Placement of fertilizer, split doses and foliar spray under specific soil climatic conditions, may increase the efficiency of fertilizers. The use of nitrogenous fertilizers may be cut down to about 50% of normal requirements, if supplemented by bulky organic manure, particularly in irrigated farming

Role of organic matter in the soil: Investigations during the last few years in India have shown that periodic addition of large quantities of crop residues to the soil by increased production of plant material through adequate fertilization with inorganic fertilizers will permit nitrogen and organic matter to be maintained at a high level Jenny and Raychaudhuri[2] concluded that fertilization with artificial nitrogen compounds is expected to enhance the yields greatly and stimulate the root system in the soil, and these will augment the soil humus and bring it to a new higher steady-state level to benefit plant growth and soil management. Efficient use of chemical fertilizers along with available bulky organic manures and crop residues and sound soil management practices will maintain the level of soil organic matter From the point of view of soil fertility, it is important to know how much of the organic matter and nitrogen are available for supplying food to the micro-organisms. The supply is considered fair when the ratio is around 20 : 1. When it is reduced to 10 : 1 organic matter is well advanced to a stage where further decomposition will be slow and release and maintenance of nitrogen at high levels is also not possible.

Bulky organic manures also contain growth stimulating and growth regulating substances. However, some materials used in the preparation of the farmyard manure, rural compost or town waste composts, contain toxic substances such as the

heavy metals zinc, copper and nickel which if present in excess in the bulky organic manure can adversely affect plant growth.

The common forms of bulky manures are :

A. Recycling animal, human, vegetation and industrial wastes.

(a) Farmyard manure,

(b) Digested cowdung,

(c) Urban compost/Municipal compost :

(i) Activated sludge,

(ii) Sewage,

(d) Composts from urban wastes, and

(e) Composts from slaughter house wastes.

B. *Greenmanure.*

A. *Recycling animal, human, vegetation and industrial wastes* :

The main source of bulky organic manure is the dung from the farm animals and the composts prepared from the urban and rural wastes In addition, the droppings of poultry birds may account for a few million tonnes. The total potential farmyard manure in India has been estimated as 10 8 million tonnes. Assuming that the availability of N, P_2O_5 and K_2O in dung/agricultural wastes is 30, 60 and 70% of that of inorganic fertilizers and the availability of nitrogen in urine is about 50% of the potential amount, the total and available N, P_2O_5 and K_2O in cattle dung, urine and farm wastes in India are given in the Table 2[1].

TABLE 2—POTENTIAL AMOUNT OF TOTAL AND AVAILABLE N, P_2O_5 AND K_2O IN CATTLE DUNG, URINE AND FARM WASTES (MILLION TONNES)

	N	P_2O_5	K_2O
Total	2 20	0 82	1.78
Available	0.78	0 49	1.32

(a) *Farmyard manure* : Farmyard manure is a very valuable material for maintaining soil fertility in its widest sense The upward trend in fertilizer prices has necessitated improvements in the storage and application of farmyard manure so as to make better use of its plant nutrient content. The common farmyard manure is produced from cattle dung, 27 kg per adult animal per day, urine, 18 kg per adult animal per day, and bedding straw estimated at 1.5 kg per adult animal per day.

The overall mean value for the composition of farmyard manure in terms of organic matter and primary and secondary plant nutrients is given in Table 3.

The *p*H of farmyard manure is usually high (8.0 or higher) due to the presence of ammonia, but when incorporated in the soil it does not greatly

TABLE 3—COMPOSITION OF FARMYARD MANURE AS PERCENTAGE OF FRESH MATERIAL*

Dry matter	Ash free dry matter	Total N	Total P_2O_5	Total K_2O	Total MgO	Total CaO
23	17	0.6	0.3	0.7	0.04	0.20

* Source : Organic Manure, Ministry of Agriculture, Fisheries and Food, London, Bulletin 210, 1976.

affect the soil *p*H. Where earliness is important particularly in vegetable crops, application of heavy dressings of farmyard manure along with chemical fertilizers usually gives better results than by using chemical fertilizers alone.

Treatment with farmyard manure increases the biological activity of the soil as is evidenced from the increased rate of evolution of carbon dioxide ; earthworm activity in soil is greatly increased, the nodulation of legumes is improved and the population of pathogens causing plant diseases is reduced.

Farmyard manure contains other nutrients including micronutrients, the average level of which is shown in Table 4.

TABLE 4—COMPOSITION OF FARMYARD MANURE (FRESH MATERIAL BASIS)

Nutrient	Content (mg/kg)
Sodium	1000
Chlorine	2000
Iron	180
Manganese	45
Zinc	20
Copper	4
Boron	4
Cobalt	0 3
Molybdenum	0.3
Iodine	0.05

Source : Organic Manure, Ministry of Agriculture, Fisheries and Food, London, Bulletin 210, 1976.

Dean[3] analysed the yield records of Pusa Permanent Manurial-cum-Rotation Experiments for selected treatments with farmyard manure, NPK, and NP which are summarised in Table 5.

TABLE 5—AVERAGE YIELD (kg/acre) IN PUSA PERMANENT MANURIAL-CUM-ROTATION EXPERIMENTS, 1930-57

Crop	Treatment			
	FYM*	NPK	NP	No Manure
Total Annual	1920	1462	1253	449
Maize	1020	656	419	213
Pigeon pea	1086	940	1076	386
Peas	584	463	477	145
Wheat	905	724	651	241
Barley	1001	1066	1090	343

*FYM was applied to supply 44.8 kg N/ha.

The yields of FYM plot have been maintained at higher level of annual production than rest of the treatments. The yields of barley and pigeon pea have been materially influenced by phosphate

applied to the soil, of peas and wheat to a slightly lesser extent. Potash appears to be limiting for the yield of maize.

(b) *Digested cowdung*: Cowdung cakes are widely used as fuel in Indian villages. The proportion of dung used for preparing cowdung cakes varies in different States in India from 30-50%. Heat efficiency of dung cakes is low and burning of cowdung cakes give rise to smoke. Further, as the cakes are used as fuel only, the plant nutrients in the dung are wasted.

Cowdung gas or biogas is the gas derived from cowdung and other natural farmyard waste by anaerobic fermentation. A biogas plant consists of a digester and a gas holder. The fuel gas from the biogas plant has the following composition :

TABLE 6

Composition of Biogas (%)

Methane	50-60
Hydrogen	5-10
Carbon dioxide	30-45
Nitrogen	1-2

The fuel gas can be used for heating or lighting or as motive power. The range of N, P_2O_5 and K_2O content of the residual slurry on dry basis is as follows :

TABLE 7

Composition of Biogas Slurry (%)

N	1.4 to 1.8
P_2O_5	1.1 to 2.0
K_2O	0.8 to 1.2

In addition, digested slurry contains a fair amount of essential micronutrients. The slurry is rich in humus and easily mixes with the soil. It prevents breeding of flies and is free from odour which is usually associated with compost manure (Biswas[4]).

It is not economic to set up even the smallest size biogas plant (2 cubic metres) unless 40 kg fresh dung is available daily. The cowdung should be mixed with equal quantity of water before it is fed into the gas plant which should be located near the kitchen in an open area exposed to the sun for a greater part of the day. The ground water level at the site should be at least 4 metres below the surface throughout the year. Besides producing fuel gas and manure, the biogas plant provides local sanitation.

Comparative advantages of cowdung composted in manure pit, cakes for fuel and dung digested in a biogas plant in one year from 45 kg of fresh cattle dung per day can be seen from Table 8 (Rao[5]).

(c) *Urban compost/municipal compost*: The urban/municipal compost from sewage purification system consists of two broad types: (i) activated sludge and (ii) sewage.

TABLE 8—COMPARATIVE ANNUAL ADVANTAGES OF UTILISATION OF 45 kg OF FRESH CATTLE DUNG PER DAY

Method of utilisation	Amount of fuel obtained	Effective heat value	Amount of manure
Composted in manure pit	Nil	Nil	7 cartloads
Converted into cakes for fuel	3.65 tonnes	1.55 million k cal	—
Digested in biogas plant	620 m³	1.87 million k cal	10 cartloads

1 cartload = 2 tonnes (approx.)

(i) *Activated sludge*: In India, as in other parts of the world, the growth of cities is on the increase and the problem of efficient utilisation of sludge and sewage is assuming increasing importance. In large cities where area for cultivation is limited some of the sewage is wasted or improperly utilised. In recent years activated sludge plants have been installed to make the best use of town wastes. The composition of activated sludge is given in Table 9 (Das[6]).

TABLE 9—COMPOSITION OF ACTIVATED SLUDGE (ON DRY BASIS)

Item	%
Loss on ignition	76.77
Mineral matter	53.23
Sand and Silica	36.74
Nitrogen	4.12
P_2O_5	2.24
K_2O	0.95
CaO	2.87
MgO	2.20
Fe_2O_3	4.96

The sludge contains approximately 50% organic matter and has C : N ratio 11.7 : 1. Of its nitrogen, 26 to 34% undergoes mineralization in 4-6 weeks as compared to 30-44% in oilcake in 6-8 weeks time. Thus its rate of mineralisation is quite high. Municipal sludge often contains undesirable chemicals which may be toxic to plant and/or eventually toxic to animals and human beings that consume edible parts of such plants.

(ii) *Sewage*: Manurial value of Poona sewage was investigated by Talati[7] and the results are given in Table 10. When directly applied to the field without sedimentation it contains about 44-53 parts per 100,000 solids, of which about 50% is organic suspension. Sewage farming is more

TABLE 10—COMPOSITION OF POONA SEWAGE (PARTS PER 100,000)

Season	Free and saline ammonia	Albuminoid ammonia	Total N	P_2O_5	K_2O	CaO	Dispersed solid
Hot weather	2.51	0.92	3.43	1.350	0.521	14.287	44.10
Monsoon	2.36	0.79	3.15	1.737	0.377	13.844	44.10
Winter	2.41	0.84	3.25	1.969	0.396	14.008	53.30

profitable when quick growing crops of leafy nature are grown. Sewage containing industrial effluent may contain zinc, copper, nickel and possibly cadmium above their toxic limits.

(d) *Compost from urban wastes*: Urban compost preparation consists in the collection of all town wastes like sweepings, garbage, household rubbish, night soil, etc. and allowing them to decompose in trenches by the Bangalore method. All these wastes when composted in trenches yield a good bulky organic manure of high quality, quite rich in fertilizing elements including micronutrients such as copper, zinc, manganese and boron. The manure so obtained is quite innocuous and safe to handle and apply to the soil. Urban compost gives very high yields of crops grown under irrigation viz., vegetables, potatoes sugarcane, rice, banana, etc. Urban compost has been used effectively for the reclamation of saline and alkali soils also.

(e) *Manure from slaughter house wastes*: Bones, bloodmeal hoof and horn-meal and meat-meal constitute the main slaughter house wastes. These provide useful sources of manure wherever available. In India the bloodmeal, hoof and horn-meal, which are at present used for manurial purposes can amount to about 0.25, 0.06 and 0.06 million tonnes per annum providing 0.025, 0.0066 and 0.0048 million tonnes of nitrogen, respectively.

B. *Greenmanure*:

Greenmanuring in irrigated tracts with adequate size of holding has been found to be beneficial in India for paddy and sugarcane. The approximate amount of nitrogen turned under by some of the greenmanure crops is given in Table 11 (Mirchandani and Khan[8]).

TABLE 11—AMOUNT OF NITROGEN TURNED UNDER BY SOME GREENMANURE CROPS

Greenmanure crop	kg N/ha turned under
Crotalaria juncea (Sannhemp)	84.0
Sesbania aculeata (*Dhaincha*)	77 2
Cyamopsis tetragonoloba (*Guar*)	62.4
Vigna sinensis (Cowpea)	56 3
Phaseolus aureus (*Moong*)	38 6

Greenmanuring has, in most parts of the world, been applied more successfully to increase the available nitrogen supply than the humus content of the soil. Thus Singh[9] has shown on the basis of the data of the Pusa Permanent Manurial tri[als] started in 1908, that greenmanuring has not resulte[d] in any great change in the organic carbon conten[t] of the Pusa soil (Table 12).

TABLE 12—ORGANIC CARBON CONTENT OF SOIL (%)

Treatment	1940-41	1947-48	1954-55	1957-58
Control	0.223	0.212	0.229	0.280
NPK	0.235	0.292	0.245	0.365
Green-manure	0.228	0.291	0 257	0.358
Green-manure + P	0.300	0.315	0.261	0.430

These data show that the content of organ[ic] carbon in the control plots has remained practicall[y] constant. Purely greenmanure plots have maintaine[d] a slightly higher organic carbon content, but th[e] plots receiving inorganic fertilizers have maintaine[d] a higher level of organic carbon. The greenmanu[re] plots receiving phosphorus, maintained the highe[st] content of organic carbon.

Yardstick of response to bulky organic manur[e]: A large number of results obtained from a numb[er] of Government farms and experimental statio[ns] show that the farmyard manure, when proper[ly] prepared, can give increased yield ranging fro[m] 10-50%. The results of All India Coordinat[ed] Agronomic Experiments Scheme averaging ov[er] 3-4 years indicate that generally, application [of] farmyard manure at the rate of 75 tonnes p[er] hectare gave increase of annual grain yield of ri[ce] and wheat in fixed rotation, ranging from 5 to [...] quintals per hectare. Much better results can [be] obtained when application of farmyard manure [is] made in combination with other practices of goo[d] management such as improved seed, prop[er] crop rotation and supplementary fertilizers. F[or] obtaining economic return, the use of chemic[al] nitrogenous fertilizers may be cut down by 50% [by] using in combination with bulky organic manure.

Environmental pollution: The promotion [of] integrated plant nutrients as outlined above wou[ld] help in solving the severe problems of environmen[tal] pollution of soil, water and atmosphere which a[re] bound to be faced as the pace of development a[nd] exploitation of resources is increased. Indeed, f[or] tackling the problem of environmental pollutio[n] there is no alternative to efficient and econom[ic] basic resource conservation measures on a natio[nal] scale.

Recent trend: In more recent years Governme[nt] of India have stressed on the usefulness of integrat[ed] nutrient supply to soils for maintaining and buildi[ng] up sustained soil productivity. The experiments [of] Professor N. R. Dhar and his coworkers at t[he] Sheila Dhar Institute of Soil Science, University [of] Allahabad, have established that application [of] organic matter along with rock phosphate fi[xes] atmospheric nitrogen in the soil and leads [to] increase in its nitrogen status. This is a cheap a[nd] convenient method of improving soil fertility a[nd] needs trials on pilot project scale in different s[oil] climatic regions. Fundamental work on differ[ent] types of bulky organic matter including gre[en] manure, rural compost, town compost, sewa[ge,] sullage and industrial wastes like press-mud e[tc.] is urgently called for.

Conclusion: The high prices of chemical fe[rti]lizers and the shortage of energy have made [it] urgent to show the farmers the way to increa[se]

productivity by using less fertilizers. A significant development in this direction is the recylcing of organic wastes. Indeed, there has been over-emphasis in the past on the use of chemical fertilizers to boost agricultural production. Use of chemical fertilizers along with organic manure would maintain the fertility of the soil and increase crop production. Field trials show that about 50% of chemical fertilizers needed on the basis of soil test could be saved in irrigated farming if used judiciously along with bulky organic manures.

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A Study of Iron Concretions in Lateritic Soil of West Bengal

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Iron concretions of various sizes are present in lateritic soils of West Bengal. The soils are acidic and free iron oxides are present abundantly. From analysis of the outer iron coating and the inner core of the concretions it appears that these have formed by leaching down of iron and manganese in the reduced state and their deposition in concentric lamination over a nucleus which is either a particle of quartz or parent material. Alternate wet and dry seasons that prevail is an essential condition for formation of these iron concretions.

IN West Bengal lateritic and red soils constitute an important soil group, covering the western part of the State. The soils are red in colour of various shades, variable in depth and iron concretions of various sizes range from thick indurated cemented mass to only a few detached particles. A study of the characteristics of these iron concretions was made to obtain their genesis, the results of which are presented in this paper.

Materials and Methods :

Four representative soil profiles from the lateritic area of West Bengal were selected for the study, all belonging to plinth paleustalf. Their morphological descriptions are given below Soil colour is under moist condition according to Munsell Colour Chart.

Profile 1.

Situated in village Pacha Dahara, P S. Bishnupur, Dist. Bankura, very gently sloping upland with normal relief, well drained, *Sal* forest with thorny plants.

A1	0-8 cm	Yellowish red (5YR5/6) loam, crumb structure, slightly hard when dry, friable when moist, sticky when wet, some iron concretions, clear and smooth boundary.
A2	8-15 cm	Yellowish red (5YR4/6) clay loam, crumb structure, hard when dry, firm when moist, sticky when wet, some iron concretions along with quartz particles, clear boundary.
B1	15-65 cm	Red (2.5YR4/6) clay loam, subangular blocky, hard when dry, firm when most, sticky when wet, many iron concretions, clear and smooth boundary.
B2	65-100 cm	Red (2.5YR4/6) clay, angular blocky, very hard when dry, very firm when moist, very sticky, clay skin on ped faces, many iron concretions, clear boundary.
C	100 cm+	Murrum mass along with hard and compact iron concretions with some soil matrix.

Profile 2.

Situated in village Kuliajan, P S. Bishnupur, Dist. Bankura, level upland with normal relief, well drained waste land, with occasional bushy shrubs.

A1	0-7 cm	Light reddish brown (5YR6/4) sandy loam, crumb structure, loose when dry, friable when moist, nonsticky, few fine roots, clear and smooth boundary.
AB	7-32 cm	Yellowish red (5YR5/4) sandy clay loam, crumb to granular structure, slightly hard when dry, friable when moist, slightly sticky, few fine roots, gradual and smooth boundary.
B2	32-90 cm	Red (2.5YR5/6) clay loam, angular blocky, slightly hard when dry, friable when moist, slightly sticky, a few iron concretions, evidence of clay skins in patches, gradual and smooth boundary.
B3	90-130 cm	As above, with many iron concretions and quartz particles.
C	130-150 cm+	Hard murrum mass with iron concretions.

Profile 3.

Situated in village Piardoba, P.S. Bishnupur, Dist. Bankura, well drained upland with normal relief, very gently sloping. Village forest but with scanty vegetation.

A1 0-9 cm Yellowish red (5YR4/6) sandy loam, crumb structure, slightly hard when dry, friable when moist, slightly sticky, a few iron concretions, clear and smooth boundary.

A2 9-39 cm Yellowish red (5YR4/6) loam, sub-angular blocky, slightly hard when dry, friable when moist, slightly sticky, a few iron concretions, clear boundary.

B1 39-58 cm Red (2.5YR4/6) clay loam, angular blocky structure, friable when moist, sticky when wet, more iron concretions, gradual boundary.

B2 58-150 cm Red (2.5YR4/6) clay, strong angular blocky, firm when moist, very sticky when wet, many iron concretions, clear boundary.

C 150 cm+ Murrum mass with many iron concretions and soil matrix.

Profile 4.

Situated in State Soil Conservation Research Farm, Midnapur, well drained level upland, formerly under cultivation, currently fallow.

A 0-15 cm Yellowish red (5YR5/6) silty loam, sub-angular blocky, hard when dry, friable when moist, sticky when wet, clear and smooth boundary.

AB 15-75 cm Reddish yellow (5YR6/8) silty clay loam, sub-angular blocky, hard when dry, friable when moist, sticky when wet, a few small iron concretions.

B2 75-120 cm Strong brown (7.5YR5/8) silty clay loam, angular blocky, hard when dry, firm when moist, sticky when wet, many iron concretions, gradual and smooth boundary.

B3 120-150 cm Reddish yellow (7.5YR6/6) silty clay loam, angular blocky, hard when dry, firm when moist, more iron concretions, clear boundary.

C 150 cm+ Weathered parent material along with iron concretions.

In all the areas granite, gneiss and occasionally schists constitute the geological rocks. Natural vegetation consists of *Sal* (*Shorea robusta*), *Palas* (*Butea frondosa*), *Babul* (*Acacia nilotica*), bamboos and grasses.

The climate of the region is characterised by hot summer months April to June, wet monsoon months July to September or October and mild winter months November to February or March. The mean annual rainfall is about 1200 to 1500 mm, about 75% of which is received during the monsoon months, the rest of the year being fairly dry. Only during the four monsoon months precipitation is *more than evaporation and wet condition results,* but during the rest of the year evaporation is more than precipitation and dry period prevails. There is thus distinct alternate wet and dry seasons in the area and ustic moisture regime prevails.

Standard methods were followed for analysis of the soil and concretion samples (Piper[1], Jackson[2]).

Results and Discussion

Morphological descriptions of the soils show that the surface horizon has yellowish red to reddish brown colour all with hue 5YR. The red colour persists in lower horizons. The texture is sandy loam to loam and silty loam at the surface which becomes some what heavier in lower layers. Dark coloured or brown, medium hard to hard, round to sub-rounded iron concretions are present in all the profiles. They are generally only a few in number at the surface but become more abundant with depth. Finally at 100 to 150 cm depth in the C horizon there is the compact layer of iron concretions, weathered parent material and soil matrix.

The more important physical and physico-chemical properties of soils are given in Table 1. All the soils are acidic. The acidity decreases with depth. The cation exchange capacity is low, and so is the organic carbon content.

The clay mineral consists dominantly of kaolinite along with some illite.

All the soils contain variable amounts of free iron oxides. Both the oxalate extractable (by method of McKeague and Day[3]) and dithionite extractable (by method of Alexander[4]) iron oxides, giving the amorphous and the crystalline oxide contents respectively increase with depth, showing their mobility down the profile (Table 2). There is a slight but distinct tendency for the active iron ratio Fe_o/Fe_d to increase down the profile, suggesting that the initial rate of release of iron from primary minerals is relatively rapid in relation to the rate of crystallisation of the secondary iron compounds. Total iron also increases with depth. Manganese content is low, but this also increases slightly in lower horizons.

The iron concretions in these soils are variable in size, being small in the upper horizons, but becoming bigger and more abundant in lower depths. The surface colour of the concretion is reddish yellow to pink and reddish brown, all with

TABLE 1—PHYSICAL AND PHYSICO-CHEMICAL PROPERTIES OF SOILS

Horizon cm	Mechanical composition %				pH	Organic C (%)	C.E.C. me/100 g	Base saturation (%)
	Coarse sand	Fine sand	Silt	Clay				
Profile 1								
0-8	31.9	29.3	17.6	21.2	5.3	0.086	2.82	22
8-15	32.4	21.9	20.8	24.9	5.5	0.047	3.32	28
15-65	37.0	18.9	13.6	30.5	6.0	0.046	4.32	41
65-100	24.3	14.8	15.6	45.3	6.3	0.043	7.78	61
Profile 2								
0-7	42.9	34.7	8.2	14.2	6.25	0.086	1.58	29
7-32	43.0	27.8	6.5	22.7	4.8	0.065	2.16	18
32-90	33.3	25.9	16.6	24.2	5.6	0.043	3.57	28
90-130	30.9	19.2	20.5	29.4	6.0	0.054	6.04	53
Profile 3								
0-9	50.0	21.0	11.2	17.8	4.8	0.113	1.96	24
9-39	42.2	21.5	14.3	22.0	5.15	0.081	3.07	33
39-58	39.5	21.2	10.8	28.5	4.45	0.054	2.70	34
58-150	40.7	16.0	8.2	35.1	5.75	0.036	4.43	49
Profile 4								
0-15	37.1	20.1	26.2	16.6	5.1	0.130	3.57	37
15-75	25.6	13.6	30.2	30.6	5.05	0.054	5.41	47
75-120	30.8	12.2	25.4	31.6	5.45	0.043	7.40	58
120-150	27.8	12.5	26.9	32.8	5.85	0.011	9.03	65

TABLE 2—IRON AND MANGANESE CONTENTS IN SOILS (%)

Horizon cm	Total iron Fe_2O_3	Oxalate extractable iron (Fe_o)	Dithionite extractable iron (Fe_d)	$\frac{Fe_o}{Fe_d}$	Total MnO
Profile 1					
0-8	5.01	0.76	1.47	0.52	0.02
8-15	8.86	0.82	1.17	0.70	0.03
15-65	10.26	1.52	2.02	0.75	0.06
65-100	10.24	1.03	1.53	0.67	0.09
Profile 2					
0-7	3.81	0.57	0.91	0.63	0.05
7-32	5.21	0.87	1.03	0.84	0.07
32-90	4.39	1.01	1.24	0.81	0.04
90-130	7.52	1.04	1.29	0.81	0.13
Profile 3					
0-9	3.61	0.63	0.89	0.71	0.06
9-39	5.70	0.88	1.21	0.73	0.05
39-58	8.56	1.13	1.49	0.76	0.07
58-150	9.60	1.50	1.75	0.86	0.12
Profile 4					
0-15	5.01	0.98	1.12	0.88	0.06
15-75	7.26	1.37	1.78	0.77	0.07
75-120	9.82	1.06	1.30	0.82	0.05
120-150	9.83	1.43	1.58	0.91	0.12

hue 5YR. On breaking the concretion the inner core was found to have reddish yellow to reddish brown and dark reddish brown colour, sometime with black specks.

The concretion has always a nucleus or central core of quartz or parent material particle or clay aggregate around which there has been deposition of iron and manganese in concentric lamination. This is clear from examination of a broken concretion under a low power microscope. Evidently, the concretion has gradually grown in size by deposition of iron and manganese oxides.

For convenience of study, the concretions were separated into two groups according to their size, namely (i) those with diameter between 2 and 5 mm and (ii) those with more than 5 mm diameter. In this study, very small concretions of less than 2 mm size were not included.

The chemical compositions of the outer coating and the inner core of the concretion were estimated. For this, concretions from each of the two groups were treated with hot 6*N* HCl so as to dissolve the outer coating and the extract was analysed for the various constituents. The results are shown in Table 3. The residue or the insoluble part left after acid extraction, may be taken as the nucleus or the core. There is very little difference between the residues from the smaller and the larger size concretions in each horizon.

TABLE 3—ANALYSIS OF HCl EXTRACT OF CONCRETIONS (% COATING)

Size nm	Insoluble %	Fe_2O_3	Al_2O_3	Mn	CaO	MgO	Na_2O	K_2O	$\frac{Fe}{Mn}$
Profile 1									
8-15 cm									
2-5	84.6	63.56	16 50	14.90	1 10	0 59	1 62	1.90	3.0
5+	88 6	58.68	13 77	23.33	0 95	0 35	1 56	1.40	1.8
15-65 cm									
2-5	90.8	54.90	12.28	23 91	2 28	1 30	3 80	1.52	1 6
5+	92.8	60.42	15.41	14 17	2 64	1 11	3 75	2 50	3 0
65-100 cm									
2-5	70 2	70 88	15.17	10 43	0 57	0 94	1 57	0 42	4.8
5+	67.6	72 54	13.31	9 98	0 71	0 18	0.95	0 35	5 2
Profile 2									
32-90 cm									
2-5	94 8	59.92	3.65	15 39	3 08	2 31	10 77	4 81	2.6
5+	94.2	63 10	7.41	20 86	1 55	0 70	3 62	2 76	2 1
Profile 3									
9-39 cm									
2-5	95 4	58.86	17.83	9 57	1 52	1 73	5 00	5.43	4 3
5+	95.0	66.60	8.60	16.60	1.20	0 40	2 00	4.60	2.8
39-58 cm									
2-5	94.8	60 00	6 34	15 77	2.70	2 11	6.16	6.90	2 7
5+	94.4	58.40	11.78	18.02	0.89	1.25	4.46	5.18	2.7
58-150 cm									
2-5	93 8	58.68	16.13	13 55	1 77	0.98	4.20	4.51	3 0
5+	94 0	62 23	16.83	9 17	1.83	2.00	3 16	4.82	4 9
Profile 4									
75-120 cm									
2-5	76 8	65.58	10 86	16 77	1.76	1 36	2 28	1.36	2.7
5+	80 0	68.95	11.90	15 00	1.15	0.60	0.95	1.45	3.2

TABLE 4—CHEMICAL COMPOSITION OF CORE OF CONCRETIONS AFTER HCl TREATMENT

Horizon cm	SiO_2	Al_2O_3	Fe_2O_3	Mn	CaO	MgO	K_2O	$\frac{SiO_2}{R_2O_3}$
Profile 1								
8-15	89 86	6.23	3 24	Tr	0 35	0 14	0.18	18 5
15-65	87.80	7.32	4 32	Tr	0.28	0 12	0.16	14 9
65-100	87 90	1.34	10 24	0 78	0 42	0 27	0.05	19.6
Profile 2								
32-90	94.97	2.43	2.04	Tr	0.26	0.24	0.06	42.8
Profile 3								
9-39	90.92	6.17	2.40	Tr	0.12	0.16	0 23	20.0
39-58	91.68	4.36	3 32	Tr	0.23	0.25	0.16	23.9
58-150	95.17	2 05	2.08	Tr	0 39	0.22	0.11	48.1
Profile 4								
75-120	91.01	2.58	5.68	0.12	0.38	0.15	0.08	24.9

In the HCl extract the total sesquioxides vary but Fe_2O_3 is always present in larger amount. There is a general trend that at lower depth of the soil more iron and manganese have deposited as concretion which are extractable by acid. Fe/Mn ratio is variable and so the proportions of iron and manganese are not related to the size of the core. Leaching down of the elements through the soil profile to form the concretion has not been uniform. TiO_2 content is extremely low. Other basic oxides are also very low and so these have no participation in the formation of the concretion.

The residue left after acid extraction was also analysed after crushing and fusion with sodium carbonate. In this case the residue of both the size groups were mixed and composite samples were made. The analytical data are presented in Table 4. In all cases the residue after acid extraction was white in colour on the outer surface.

It may be concluded that the core over which the concretion has formed is made up largely of quartz particle or may be a particle of the parent material.

Conclusion: Depending upon the characteristics of the iron concretions classification have sometimes been suggested by some workers. Pawluk and Dumanski[5], working on a poorly drained soil of Alaberta found the concretions localised in the zones of strongest mottling and were more abundantly distributed in A than in B horizon.

Iron concretions in the lateritic soil of West Bengal under study are irreversibly hard particles, rounded to sub-rounded in shape, the size increasing with depth.

In the formation of the soil abundant rainfall, but with alternate wet and dry conditions and oxidising and reducing changes under free internal drainage have resulted in leaching down of iron by solubilisation by its reduction into ferrous state and its subsequent precipitation in the ferric form in the lower part of the soil profile. A nucleus for such deposition in lamination or concentric form is essential which is either a quartz or a parent rock particle. Manganese also moves along with iron for formation of the concretion. The rates of movement of iron and manganese are, however, variable, as has already been discussed. There are several conditions favourable for deposition of iron and manganese by arrestment of their downward movement and oxidation. These are changes in soil *p*H, change in redox potential, dry oxidising state or also may be the fluctuation of ground water level. It, however, needs to be stressed that the essential condition for formation of the concretions is that the soil profile must be saturated with water at some season. Alternate wetting and drying as occurs in the lateritic area have resulted in their irreversible hardening.

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Maximizing Crop Yields

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AT the time of our independence we had the capacity to produce about 50 million tonnes of food grains per year. This has now enhanced to over 130 million tonnes per year, besides increasing production of fruits, vegetables, tubers, cotton, jute, plantation crops etc. But in course of the next 20 years we have to increase our capacity to 230 million tonnes per year to feed the population of estimated over 900 million. On the other hand we find that almost every day acres of fertile land being taken away for dwelling and industrial purposes. Increasing deforestation, soil erosion and land degradation is also reducing the crop production potential of the land. The only way left is to improve soil fertility and to increase production per unit area per unit time. This has been the philosophy of the school lead by Prof. N R. Dhar for the last half a century. He has been a leading advocate of energy conservation farming and recycling of agricultural wastes for enriching the soil and increasing production without much input of fossil fuel energy. His warning however, went unheeded till the recent energy crisis has clearly shown that food production is very vulnerable to an interruption of oil supplies and total energy inputs. The following table shows a comparison of energy input and return in modern high yielding maize production vis-a-vis in the age old practice of hand or bullock powered maize production.

	Energy input k cal per ha	Output/input ratio
Machine produced high yielding maize	86,66,910	216 : 1
Hand powered maize	52,762	1282 : 1

Thus, modern methods of obtaining high yields appear rather inefficient Can we increase the efficiency of food production without the use of massive energy use ? I think it is possible to maximize yield and increase the efficiency of agriculture by scientific manipulation of crop environment and efficient use of our renewable resources If human ingenuity can place a man on the moon there should be no reason why it cannot solve the food problem.

Efficiency of crop production · The word efficiency is often used to connote performance. Thermodynamically, efficiency is the output of useful energy from a system expressed as a fraction of the

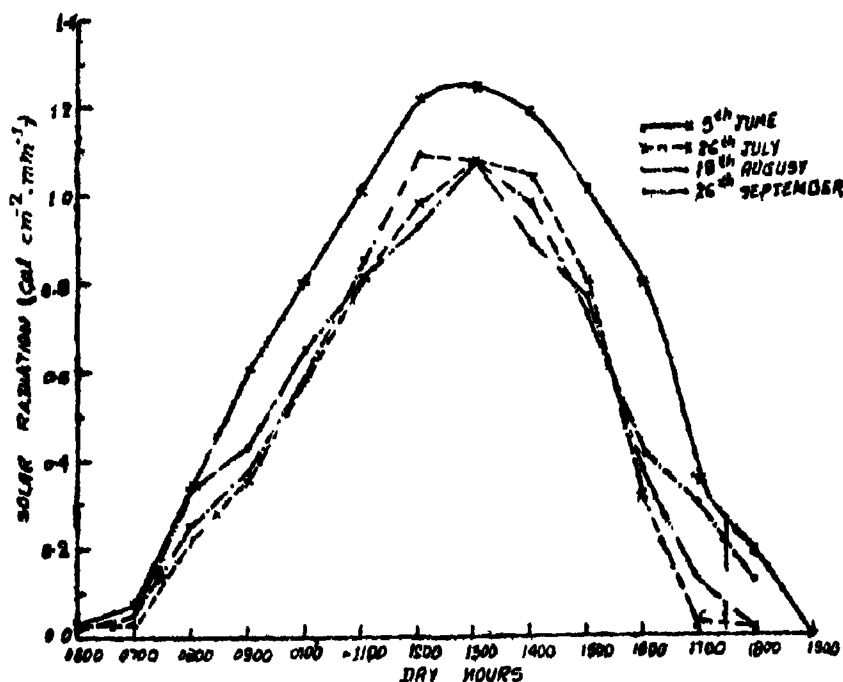


Fig. 1. Daytime hourly variations in solar radiation flux density

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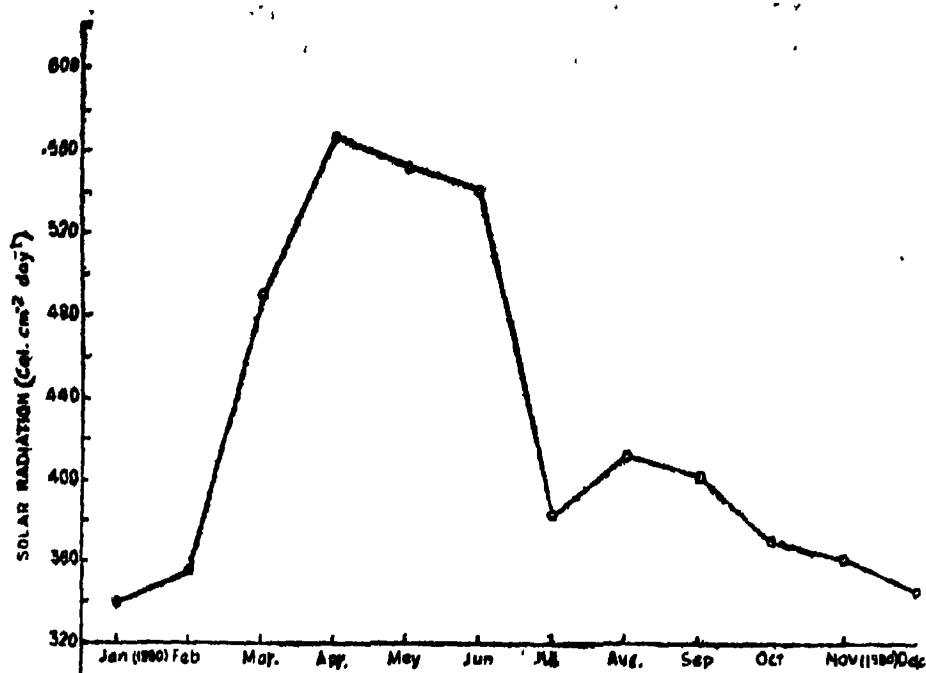


Fig. 2. Annual variations of solar radiation flux density.

energy input. In crop production, the energy stored by photosynthesis in organic compounds is an useful output from a system which has solar energy as its input.

Energy environment of crops: CO_2 from air, water, and mineral nutrients from soil are the raw materials used by plants to manufacture food with the help of solar radiation. Solar radiation is absorbed by the photosynthetic machinery of green chloroplasts and is used to reduce CO_2 to carbohydrates. The rate of photosynthesis depends on many internal and external factors. Photosynthesis includes photochemical, biochemical and thermochemical reactions which are light as well as temperature dependent. Diurnal changes in solar radiation may change the short-term photosynthesis rates. Fig 1 shows the diurnal variations in solar radiation at Pantnagar which explains how photosynthesis rate will vary throughout the day. Fig. 2 shows monthly variation in solar radiation at Pantnagar. The distribution of solar energy shows that there are sharp changes in the energy received. During April or May more than 550 cal cm^{-2} day^{-1} are received while during cloudy winters it may be as low as 340 cal cm^{-2} day^{-1}. Even in July it may be 420 cal cm^{-2} day^{-1} due to cloudy weather. The peak rate of solar radiation is received during 1200 to 1300 hrs and may reach 1.3 cal cm^{-2} hr^{-1} in June. In bright sunlight the leaves are saturated with light and the rate of photosynthesis is independent of light intensity because it becomes limited by physical and biochemical processes within the leaf.

The energy environment of plant can be described by the energy conservation equation,

Net rate of incoming energy per unit area	Net rate of outgoing energ per unit area

$$(Sr+SS)S+R+LE+G+P+M=O$$

Sr=reflected sunlight, SS=Scattered sunlight
S=Solar radiation flux

R=Thermal radiation flux Ground (Rg), atmos phere (Ra) and surrounding objects

L=Latent heat of evaporation

E=Rate of evaporation

G=Sensible heat flux by conduction from grou to surface

C=Sensible heat flux by convection in air

P=Photosynthesis

The complexity of the energy exchange with I transformation is shown in Fig. 3. Energy will flo to or from plant by radiative transfer or b conduction along a temperature gradient or by mas flow by convection. Similarly water vapou CO_2, O_2 will flow to or from the plant along concentration gradient and N will determine th size of the photosynthetic apparatus.

Energy transfer in plants: Plants on earth through evolution, have adapted uniquely to th frequency distribution of solar radiation. Ever plant is coupled to the radiation environment to different degree i.e., it absorbs, reflects and transmit the incident radiation depending upon the natur of spectral radiation and the spectral characte istics of leaves, plant shape and leaf orientation The spectral absorbance and reflectance curves fo the rice plant show that they possess hig

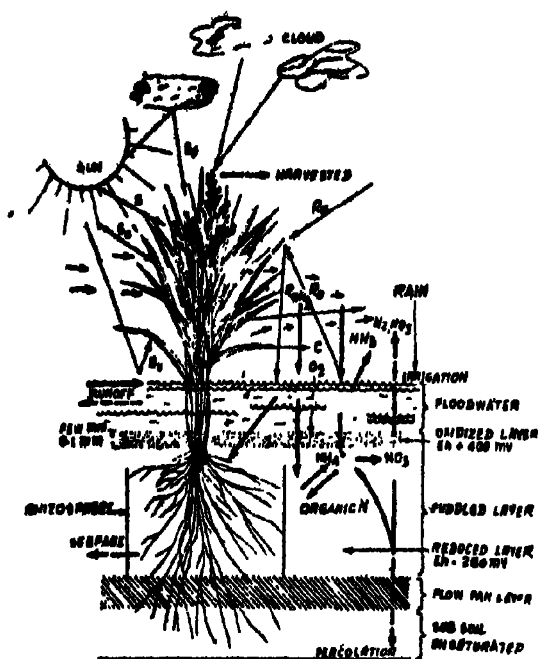


Fig. 3. Schematic diagram of energy environment and N cycling in soil-rice ecosystem.

absorbance at blue and red end of the visible wave lengths where they absorb solar radiation efficiently for maximum photosynthetic efficiency.

The complete steady state energy budget expression for a plant leaf, when there is some wind movement and when conduction term, storage term and metabolic energy are neglected is :

$$Q_{abs} = \epsilon\sigma T_s^4 + k_s\left(\frac{V}{D}\right)^{\frac{1}{3}}(TS - T_a) + L(T_s)\frac{Sp_l(T_s) - rh\, Sp_a(T_a)}{r_l + r_e}$$

Q_{abs} = Total amount of incident radiation absorbed by the plant surface,

ϵ = Emissivity for far infrared is 0.95 to 0.97,

σ = Stefan-Boltzman constant— 8.13×10^{-11} cal cm^{-2} $°K^{-4}$ min^{-1},

T_s = Surface absolute temperatur,

k_s = Convection constant depending upon size, shape and orientation of surface and nature of flux,

$S_{pa}(T_a)$ = Water vapour density of air at saturation at air temperature, "

$r_l + r_e$ = Internal and external diffusion resistances,

$L(T_s)$ = Latent heat of evaporation as a function of leaf temperature (580 cal gm^{-1} at 30°),

$Sp_l(T_s)$ = Water vapour density within the substomatal cavity,

rh = Relative humidity,

D = Characteristic dimension (width) and

V = Wind speed.

It is seen that both environmental and plant factors interact. The environmental factors are radiation, wind speed, air temperature and relative humidity. The plant factors are absorptivity to each flux of radiation, the areas exposed to radiation and total leaf area, the leaf dimension, shape, orientation and internal diffusion resistance or stomatal geometry For any combinations of the environmental and plant factors specific leaf temperature and transpiration rate can be obtained This shows that environment and plant interactions are complex and consist of a temperatue surface in a multidimensional space.

Fig 4 shows diurnal soil-plant-atmosphere temperature variation in a wheat crop on 16th Jan., 1981. It is seen that there is considerable variation in soil-plant-atmosphere temperatures throughout the day. Upto 10 cm soil depth the temperature fluctuations are very large while there is little change in temperature at 30 cm soil depth. Inside the crop near ground the diurnal changes are considerable in this study and the amount of assimulate respond over the whole growing season is taken as a constant fraction of the accumulated photosynthesis.

Yield analysis : The yield of a crop is determined by the response of physiological processes to the state of the environmen'. We have seen that this relationship between physical environment and biological response is exceedingly complex.

The yield of a crop can be expressed as :

$$Y = Cm \times f \times t \times h$$

Y = economic yield,

Cm = Maximum rate of dry matter production achieved during the main growth period,

f = Ratio of crop growth rate expressed as mean value for the whole growing season to the maximum rate obtained mid-season,

t = Time from emergence to hervest-length of growing season, and

h = harvest index.

Many experiments with crops have demonstrated a close relationship between photosynthesis rates and solar energy income[1]. This relationship depends on the spatial and angular distribution of leaves and on insolation and day length. However, the rate of dry matter production by crops especially during early growth phases is proportional to the percentage of radiation intercepted by the crop canopy.

It appears that growth rates can be calculated as the product of two factors.

a. An estimate of the maximum rate of dry matter production for a crop intercepting all the incident radiation.

b. An estimate of fraction of intercepted radiation derived from the knowledge of the leaf area index and leaf geometry.

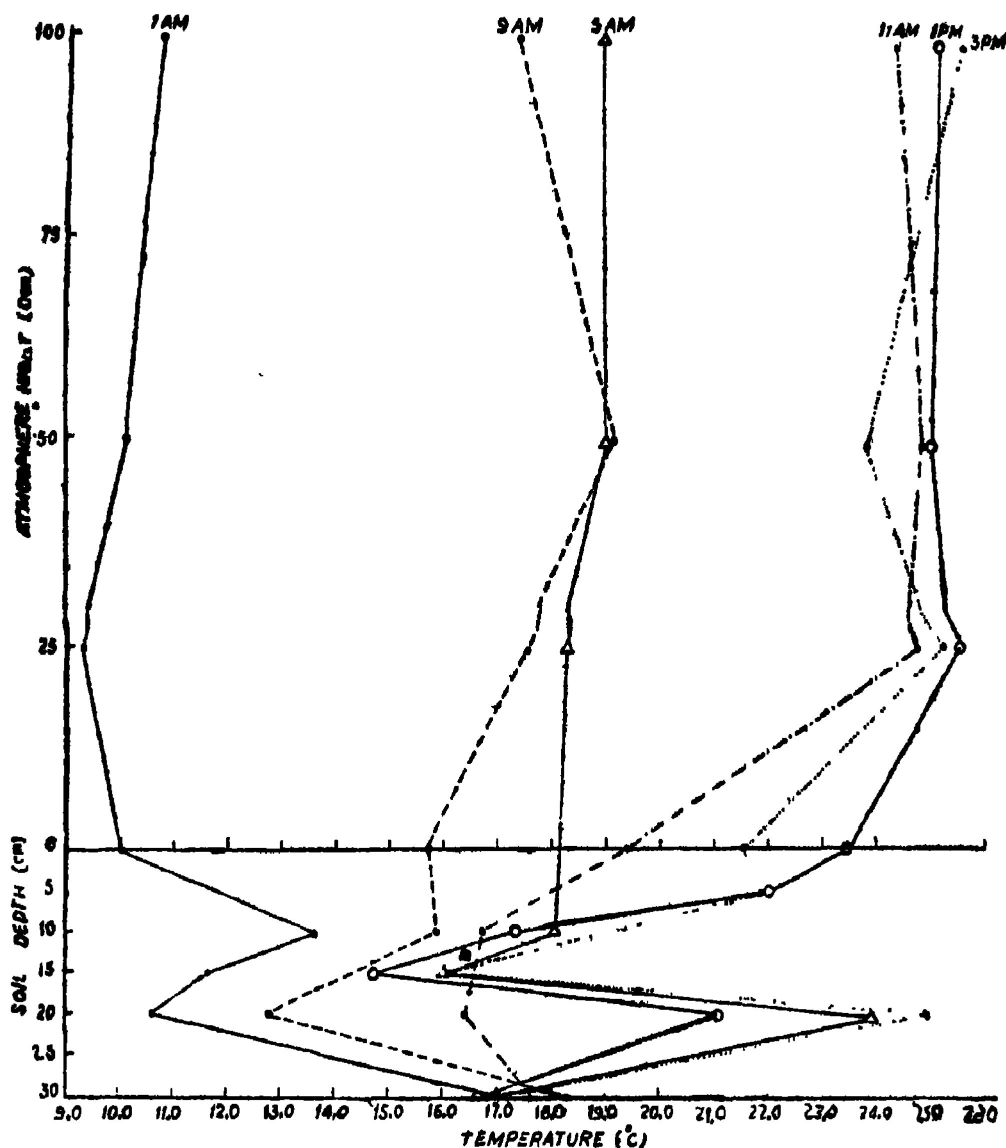


Fig. 4. Vertical temperature profile in spas.

This method tested on a series of crops in tropics and subtropics give close agreement between measured and estimated rates of drymatter production within the limits of errors of crop sampling. Since the rate at which a crop accumulates drymatter represents a balance between the rate of production by photosynthesis and the rate of consumption by respiration, in this study the amount of assimulate respired over the whole growing season is taken as a constant fraction of the accumulated photosynthesis.

Since the analysis shows that the rate of dry matter production by any crop should be proportional to the amount of light intercepted by its foliage, any method that increases light interception should help in increasing yield. This can be achieved through several ways.

(i) Breeding of varieties with faster rate of photosynthesis in brighter light.

(ii) Maintaining a maximum value for the efficiency of leaf photosynthesis in weak light as in rainy season and cloudy winters. Any stress, water, oxygen, nutrient deficiency or pests and diseases reduce this efficiency and hence of importance for optimum crop management practices.

(iii) Breeding and selection of varieties with leaves which expand more quickly and senesce more slowly. Also maintaining good emergence and maintaining initial soil fertility for quick growth of leaves.

(iv) Lengthening of growing season.

(v) Increasing harvest index.

(vi) Increasing CO_2 concentration in air.

When leaves of crop plants are exposed to bright sunlight they assimilate CO_2 from the atmosphere at a rate nearly proportional to its concentration. Though CO_2 concentration fluctuates daily and seasonally, the annual average is about 320 volumes per million or 0.6 g/m^3. If the maximum daily assimilation is about 20 g of CO_2 per m^2 of field area, all the CO_2 in a column of air 33 m tall would be used. It is therefore possible that during active photosynthesis during bright light as in India CO_2 may be deficient. It may be mentioned here that man's industrial activity is increasing the mean global concentration of CO_2 at about $1/10^6$ (by volume) per year.

(vii) Improving plant architecture and planting density.

Some 20 percent of the absorbed solar energy can be converted into plant material. This is a very good achievement for the photosynthetic machinery, so fragile and using a source of energy as fleeting as sunlight. But on farmers' field photosynthesis seldom converts more than 1% of the solar energy available during the growing season into economic yield. In the recently developed high yielding varieties of wheat and rice, plant architecture has been modified so that plants do not shade each other and promote better light interception. Dwarf maize varieties with smaller tassel, high nitrate reductase activity and upper placement of ear can respond to a population density of about 150,000 plants per hectare. Even such efficient crops now photosynthesize at only about half their potential.

Major scientific break-through during 1950s in the understanding of the photosynthetic process has been followed by research designed to increase photosynthetic efficiency of plants by better understanding plant environment interactions and also application of chemicals. For example CO_2 gas in green house or dry ice in open field have substantially increased the crop yields However, much more efficient application techniques need to be developed

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^{32}P Tracer Investigation on Phosphorus Utilization by Soybean in Vertisol

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A pot culture experiment was carried out with four levels of phosphorus using ^{32}P tagged superphosphate (viz. 0, 40, 80 and 120 kg P_2O_5/ha) and three varieties of soybean namely Punjab-1, JS-2 and Gaurav to study the uptake and utilization of applied fertilizer phosphorus in vertisol of Jabalpur. Dry matter yield, total P uptake, and percent P derived from fertilizer increased significantly with increasing levels of phosphorus. But percent utilization of added P showed a reverse trend, at all the stages of crop growth. Grain and straw yield at harvest increased significantly with increasing P levels in all the three varieties.

IT is well known that when phosphate fertilizers are added to vertisol, which are fine to fine textured soils with more than 35% clay having montmorillonite as predominant clay mineral, the phosphorus reacts with soil and gets fixed and only a small fraction of it remains in the available form. The present study was undertaken to investigate the comparative and combined effect of phosphorus on utilization by different varieties of soybean at various stages of growth in a vertisol.

Experimental

The experiment was conducted in the pot house of the department of Soil Science and Agricultural Chemistry, J. N. Krishi Vishwa Vidyalaya, Jabalpur with 3 varieties of soybean and 4 levels of phosphorus in *kharif*, 1980. Soil samples were collected from experimental area and filled in 10 kg capacity pots. The soil contained 0.6% organic carbon and 240, 10 and 268 kg/ha available N, P and K_2O, respectively. The *p*H of the soil was 7.2. A basal application of 20 kg N and 40 kg K_2O was applied at the time of sowing. Urea, single superphosphate and muriate of potash were used as the source of N, P and K respectively.

Soybean varieties, Punjab-1, JS-2 and Gaurav were chosen as the test crop. Four levels of phosphorus viz. 0 (control), 40, 80 and 120 kg P_2O_5/ha were used as tagged superphosphate having specific activity of 0.4 mCi/g P_2O_5 which was procured from Bhabha Atomic Research Centre, Trombay. The radio-active phosphorus in plant materials was determined by the method of Mackenzie and Dean[1]. Counting for radio-active P was done by placing the sample under identical geometric conditions in Geiger Muller counter. The total P uptake was determined by the method of Koenig and Johnson[2].

Results and Discussion

It is evident from Table 1 that the total phosphorus uptake increased significantly with increasing level of phosphorus at all stages of growth in all the varieties. This might be due to the higher availability of P with increasing P levels. Similar findings were also reported by Ham and Caldwell[3] and Gate and Muller[4].

The data revealed (Table 2) that the percent phosphorus derived from fertilizer increased

TABLE 1—EFFECT OF PHOSPHORUS LEVELS ON TOTAL P UPTAKE (mg/pot) BY SOYBEAN AT DIFFERENT STAGES OF GROWTH

P levels kg P_2O_5/ha.	30 DAY STAGE				FLOWERING STAGE				HARVESTING STAGE GRAIN				HARVESTING STAGE STRAW			
	Punjab-1	JS-2	Gaurav	Mean	Punjab-1	JS-2	Gaurav	Mean	Punjab-1	JS-2	Gaurav	Mean	Punjab-1	JS-2	Gaurav	Mean
P_0	6.19	7.75	6.36	6.93	16.58	16.50	18.80	17.29	48.47	52.71	47.91	49.69	6.90	5.86	5.36	6.04
P_{40}	10.34	9.73	9.22	9.76	22.84	25 46	26.89	24.96	68.32	70.05	66.31	68.22	9.41	8.08	8.55	8.68
P_{80}	11.97	12.12	10.97	11.68	34 01	34.73	31.71	33.48	85.46	90.09	85.90	89.15	12.07	11.75	11.06	11.64
P_{120}	12.69	13.49	12.17	12.78	36.43	40.60	39.34	38.79	103.80	103.53	96.55	101.29	13.99	23.26	13.27	13.50
Mean	10.29	10.77	9.80		27.46	29.32	29.11		76.61	79.10	74.16		10.59	9.73	9.56	
Effect	P		V		P		V		P		V		P		V	
S.Em ±	0.38		0.33		0.67		0.58		1.97		1.70		0.44		0.38	
C.D. at 5%	1.13		NS		1.94		1.68		5.73		NS		1.29		NS	

TABLE 2—EFFECT OF PHOSPHORUS LEVELS ON PHOSPHORUS DERIVED FROM FERTILIZER (%) BY SOYBEAN AT DIFFERENT STAGES OF GROWTH

P levels kg P_2O_5/ha.	30 DAY STAGE				FLOWERING STAGE				HARVESTING STAGE							
									GRAIN				STRAW			
	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean
P_0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
P_{40}	22.86	21.02	20 47	21 45	40.23	40 43	39 79	40 15	22 91	21 74	21 81	23 82	28 32	33 12	30 83	30 75
P_{80}	26.16	32.42	27.36	28 65	46.82	47 61	47.17	47 20	32 66	30 78	32 93	32 12	33 10	38 41	37 19	36 23
P_{120}	30.65	35.84	43.48	32.99	52.31	51 38	49 96	51 21	33 14	36 74	33 41	36 10	39 05	39 35	38.77	39 05
Mean	26.55	29.76	26.77		46 65	46.47	45 64		31 24	29 75	31 05		33 49	36 96	35.59	
Effect	P		V		P		V		P		V		P		V	
S.Em ±	0.86		0 86		0 57		0.57		0 80		0 80		0.93		0 93	
C.D. at 5%	2 55		2.55		1.72		NS		2 40		NS		2 78		NS	

TABLE 3—EFFECT OF PHOSPHORUS LEVELS ON P UTILIZATION (%) BY SOYBEAN AT DIFFERENT STAGES OF GROWTH

P levels kg P_2O_5/ha.	30 DAY STAGE				FLOWERING STAGE				HARVESTING STAGE							
									GRAIN				STRAW			
	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean
P_0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
P_{40}	2.65	2.30	2.12	2.35	10 37	11 59	11 86	11 28	17 62	17 08	19 81	18 17	2 99	3 02	2 96	2 99
P_{80}	1 75	2 20	1 62	1.85	8 91	9 30	8 41	8 87	15 67	15 62	15 84	15 71	2 24	2 53	2 29	2 35
P_{120}	1 48	1.81	1.52	1.60	7 14	7 82	7 31	7.42	14 97	14 25	12 07	13 76	2 04	1 96	1 91	1 97
Mean	1.96	2.10	1.75		8.80	9.57	9 20		16 09	15 65	15 91		2 42	2 50	2 39	
Effect	P		V		P		V		P		V		P		V	
S.Em ±	0.071		0 071		0.262		0 262		0 430		0 430		0 129		0 129	
C.D. at 5%	0 21		0.21		0 77		NS		1 27		NS		0 38		NS	

TABLE 4—EFFECT OF PHOSPHORUS LEVELS ON SOIL P UPTAKE (mg/pot) BY SOYBEAN AT DIFFERENT STAGES OF GROWTH

P levels kg P_2O_5/ha.	30 DAY STAGE				FLOWERING STAGE				HARVESTING STAGE							
									GRAIN				STRAW			
	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean
P_0	6 19	7.75	5 86	6 60	16 58	16 50	18 80	17 29	48 47	52 71	41 91	47 69	6 90	5 88	5 36'	6.04
P_{40}	7.08	6.69	7.33	7 36	13 63	15 15	16 01	14 93	52 66	54.88	48 70	52 08	6 75	5 39	5 92	6 02
P_{80}	8 84	8 18	8 05	8 35	18.17	18 19	16 74	17 70	57 59	62 65	57 73	59 32	8 09	7 24	6 98	7 43
P_{120}	9.00	8 64	8 65	8 76	17.39	19 74	19 83	18 98	64 28	65 18	64 35	64 60	8 53	8 10	8 16	8.26
Mean	7.77	8 06	7.47		16 44	17 39	17.84		55 75	58 85	53 17		7 56	6 65	4.58	
Effect	P		V		P		V		P		V		P		V	
S.Em ±	0 31		0 27		0.47		0 40		1 83		1 59		0 34		0 30	
C D. at 5%	NS		NS		1 37		NS		NS		NS		NS		NS	

TABLE 5—EFFECT OF PHOSPHORUS LEVELS ON DRY MATTER PRODUCTION OF SOYBEAN AT DIFFERENT STAGES OF GROWTH (g/pot)

P levels kg P_2O_5/ha.	30 DAY STAGE				FLOWERING STAGE				HARVESTING STAGE							
									GRAIN				STRAW			
	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean	Pun-jab-1	JS-2	Gau-rav	Mean
P_0	3.53	4.33	3.73	3.86	8.06	7.52	8 37	7.98	8.47	9.19	8.97	8.37	11.22	10.17	9.65	10.41
P_{40}	5 21	4.53	4.10	4.61	9 76	10.27	11 18	10.40	10 63	10 32	10 02	10 32	12 94	11 96	12.09	12.33
P_{80}	5.67	5.35	4.56	5.19	11.66	12 06	11 80	11 84	11 54	11 94	11 57	11 68	14 57	14 55	13.78	14.30
P_{120}	5.73	5.47	5.11	5.43	11 55	12 65	12.34	12 18	12.54	12 39	12 34	12 42	15 41	14 93	14.76	15.03
Mean	5.03	4.92	4.37		10 25	10 62	10.92		10 79	10 96	10.72		13.53	12.90	12.62	
Effect	P		V		P		V		P		V		P		V	
S.Em ±	0.14		0.12		0.26		0 22		0 24		0 21		0 22		0.19	
C.D. at 5%	0.41		0.35		0.75		NS		0 71		NS		0.65		0.57	

significantly with increasing level of phosphorus which might be due to the fact that the more the phosphatic fertilizers added to soil, the more the crop removal. On the other hand the P fixation capacity of soil being limited, an additional amount of P fertilizer added increased the pool of available phosphorus from which P was proportionately absorbed by the plants.

The percent utilization of phosphorus (Table 3) decreased significantly with increasing level of phosphorus at all the stages of growth in all varieties, which means that the utilization of added P was not in proportion to applied P level. On the other hand with lower dose the available amount of P was less than the need of the crop for its growth, as a result of which the efficiency of utilization of applied fertilizer P is high at low dose and low at higher dose. Similar results were also reported by Sinha *et al*[5], Negi *et al*[6], and Sinha *et al*[7].

The data presented in Table 4 revealed that as the dose of phosphorus increased, the uptake of P from soil source also increased at all the growth stages. This might be due to the proportionately higher uptake of phosphorus with increased dry matter yield of crop as well as better root system development caused by phosphorus application which enabled the plant to exploit the P from soil to a greater extent. Similar findings were also reported by Sinha *et al*[7].

From the results presented in Table 5 it is observed that the dry matter yield of soybean increased at all the stages of growth with increasing level of P. This increased yield was due to the response of P over control indicating that the soil was not in a position to supply enough P as required by the crop and as soon as the phosphorus deficiency was made up, increased yield was obtained. Similar results were also reported by Mahajan and Bisen[8].

In conclusion we can say that application of increasing doses of phosphate fertilizer brings about increased uptake of P by the plant, increased dry matter yield and increased uptake of P from soil source. The phosphorus derived from fertilizer also increases but percent utilization of applid Pe decreases indicating thereby that the efficiency of P utilization is more at lower level of fertilization than at higher doses.

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Movement and Transformation of Anhydrous Ammonia in Field Soil

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Movement of ammonia under the experimental condition was found to be within 3.7 cm radius from the line of injection and this was associated with rise of *p*H of the soil. After 22 days of application, this *p*H however approached its original value. Trasformation of applied NH_3 to NO_3 started from the periphery of the horizontal cylindrically shaped ammonia retention zone and it approached the point of injection. Appreciable nitrification started only after 7 days of ammonia application. Initial slow nitrification suggests preplanting application of anhydrous ammonia in dry field and then incorporation of irrigation water within 7 days without appreciable loss of added nitrogen through leaching of nitrate.

THE use of anhydrous ammonia (82 2% N) as a source of nitrogen to soil application and study of its behaviour started long back in the west[1] but no systematic work has been done in eastern countries Due to its high alkaline nature unlike any conventional solid nitrogenous fertilizer anhydrous ammonia creates an alkaline zone in the soil at the immediate vicinity of its point of application. The rise in *p*H as well as accumulation of NH_3 at this particular zone affect the soil nitrifying organisms resulting in some change in the nitrification rate in anhydrous ammonia treated soil as compared to soils treated with conventional nitrogenous fertilizers[2] Nitrification is most favourable in neutral to slightly alkaline soil[3] i.e between *p*H 7 to 8. The high *p*H and the high concentration of ammonia and ammonium resulting on the application of anhydrous ammonia are toxic to soil-microbes and cause partially sterilised condition at the maximum retention zone Accordingly, nitrification starts around the periphery of the horizontal cylindrically shaped zone of ammonia retention and then proceeds towards the point of injection[4].

The present study was undertaken with a view to understand the distribution pattern of applied anhydrous ammonia as well as its nitrification rate in field soil at Rice Production Training Institute, Hindustan Fertilizer Corporation, Durgapur, West Bengal in order to find out the possibility of use of anhydrous ammonia as a fertilizer for upland row crop as well as lowland paddy cultivation under Indian soil climatic conditions.

Materials and Methods :

The land of the experimental site was first well prepared for the application of anhydrous ammonia. Anhydrous ammonia was applied by an applicator, designed and fabricated by Markstig, Denmark, at a depth of 11.5 cm. The dose was fixed by a nitrometer fitted at the top of the applicator. The applicator was pulled by a tractor. During application, ammonia was pushed through the sharp spring loaded nozzles into the soil and the lines of injection were covered with soil very quickly by trailer harrow.

Several lines of injection were marked with pegs above the soil Periodical estimations of *p*H, ammoniacal, nitrite and nitrate-nitrogen were done on samples drawn from different depths as well as from different horizontal distances from the line of injection upto 98 days after application The soil samples were collected by cutting pits and exposing vertical surface at an angle of 90° with the line of injection The exact depth and line of injection was found out by using filterpaper soaked with Nessler's solution Soil samples were collected from different distances vertically (both upward and downward) and laterally from the point of injection on the cut perpendicular to the line of injection, by stainless steel soil sampler of 2 5 cm diameter. Samples were taken in weighed conical flasks with 50ml extractant, immediately after sampling in the field, and the weight of soil sample was determined from difference in weight Moisture percentage was determined at different depths separately *p*H was measured with an Elico *p*H meter model L 1-10 with soil water ratio 1 : 2 Ammonical and nitrite nitrogen were extracted with 2*M* KCl solution[5] Nitrate nitrogen was extracted with $CuSO_4$ Ag_2SO_4 extractant from separate soil samples[6] NH_4-N was estimated colorimetrically by Nessler's method, NO_2-N by α-napthylamine sulphanalic acid method and NO_3-N by phenyl disulphonic acid method Colour intensities were measured by photo electric colorimeter at wave lengths 420 mμ, 540 mμ and 420 mμ, for NH_4-N, NO_2-N and NO_3-N, respectively Soil temperature at a depth of 11 5 cm was also recorded

The soil of the experimental site is loamy. Its general characteristics is given in Table 1. Vertical

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TABLE 1—GENERAL CHARACTERISTICS OF THE SOIL

	Percentage (oven dry basis)
Sand	78.8
Silt	3 2
Clay	18.2
Organic C	0.55
Total N	0 056
Available N	0 015
Available K (ppm)	63.7
Cation exchange capacity (me/100 gm)	11 4
Conductivity (m mhos/cm²)	0 098
*p*H	5.1

changes of *p*H, NH_4^+-N and NO_3^--N are shown in Figs. 1, 2 and 3 respectively. Figs. 1A, 2A and 3A show the lateral changes of *p*H, NH_4^+-N and NO_3^--N respectively. Recorded soil temperature at the injection depth 11.5 cm varied from 24° to 17° during the period under study. Soil moisture at 11.5 cm depth varied from 8-12%.

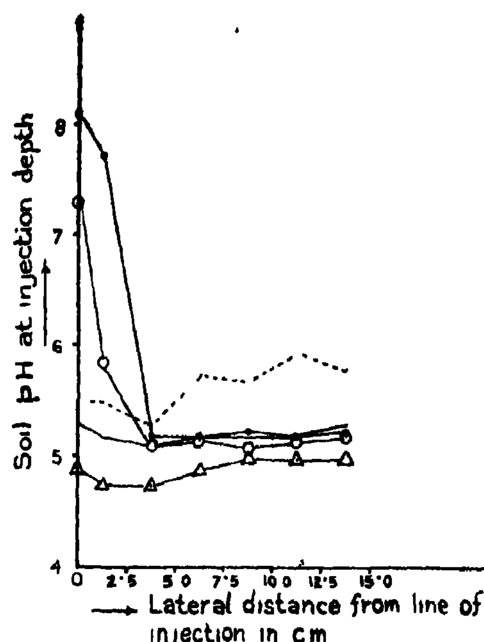


Fig. 1A. *p*H Changes in soil (lateral).
——— before application
●—● 2 days after application
⊙—⊙ 7 „ „ „
Δ—Δ 22 „ „ „
- - - - - 98 „ „ „

Results and Discussion

Changes of soil p*H* : The immediate effect of anhydrous ammonia application was rise of *p*H at the centre and immediate vicinity of the line of injection. Just at the line of injection, *p*H increased upto 8.1 from 5.3 after 2 days and movement of ammonia was upto 3.8 cm both vertically and laterally. From Figs. 1 and 1A it is clear that after 22 days, *p*H of the soil returned more or less to its original value.

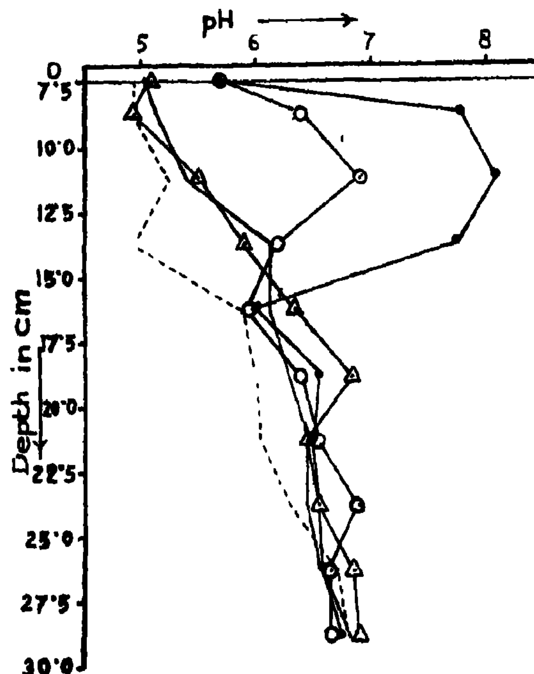


Fig 1. *p*H Changes in soil (vertical)
——— before application
●—● 2 days after application
⊙—⊙ 7 „ „ „
Δ—Δ 22 „ „ „
- - - - - 98 „ „ „

After 98 days *p*H decreased even below the original *p*H, depthwise upto 20 0 cm. From Fig. 1A it is evident that lowering of *p*H was maximum after 22 days. After 98 days *p*H was relatively higher at all distances from the line of injection laterally. This may be due to leaching of nitrate to higher depths due to rainfall. Upto 22 days there was no rainfall while between 22 days and 98 days intermittent precipitation took place. From the *p*H curves it is revealed that under the experimental condition movement of applied anhydrous ammonia has not been more than 4 cm from the line of injection, both vertically and horizontally.

Changes of ammoniacal nitrogen : Changes of ammoniacal nitrogen concentration due to anhydrous ammonia application have been shown in Fig. 2 and 2A. Localized accumulation of applied NH_3 within 4 cm radius from the line of injection was observed. After 2 days of application the highest concentration of NH_3 at the line of injection was 1068 ppm while at 2.5 cm distance it varied from 433 to 451 ppm both laterally and vertically. Exchangable ammonia was apppreciably high on the line of injection throughout the period under study though it decreased with time. Presence of NH_4^+-N at greater depths was not observed except after 98 days (Fig. 2) when appreciable accumulation of ammonia (197 ppm) was recorded at 22.5-25.0 cm depth. This might be due to leaching of nitrate from above due to rainfall and subsequent reduction to ammoniacal form.

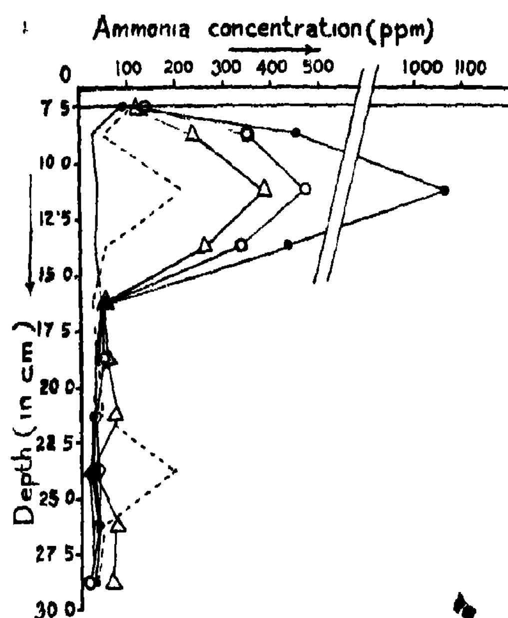


Fig. 2. Vertical movement of ammonium nitrogen.
—— before application
●—● 2 days after application
⊙—⊙ 7 „ „ „
△—△ 22 „ „ „
- - - - 98 „ „ „

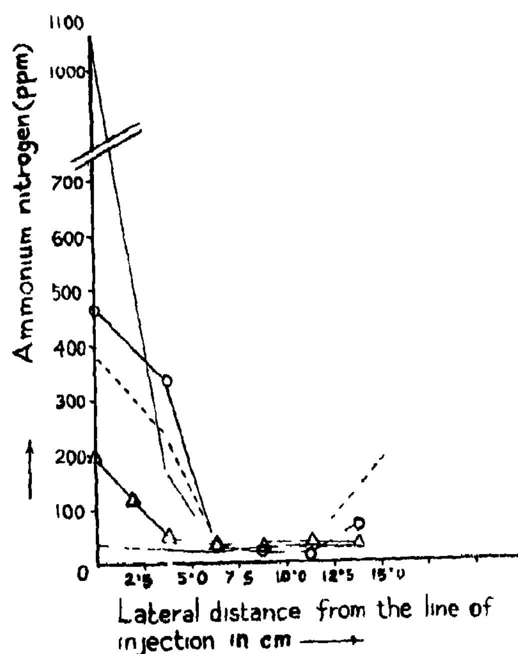


Fig. 2A. Lateral movement of ammonium nitrogen.
—— before application
●—● 2 days after application
⊙—⊙ 7 „ „ „
△—△ 22 „ „ „
- - - - 98 „ „ „

Changes of nitrite-nitrogen : Estimation of nitrite nitrogen was made depthwise as well as laterally. No accumulation of nitrite was observed at any point. Even at the line of injection accumulation of nitrite was very little or no nitrite was recorded.

Changes of nitrate-nitrogen : In Figs. 3 and 3A vertical and lateral distribution of nitrate nitrogen

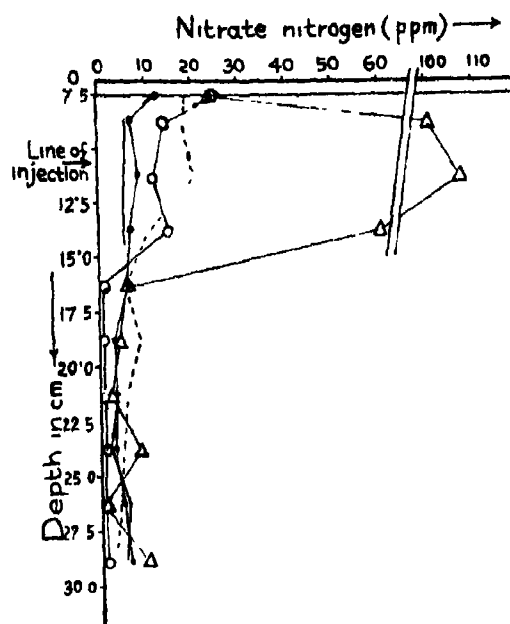


Fig 3. Changes in nitrate nitrogen concentration (vertical).
—— before application
●—● 2 days after application
⊙—⊙ 7 „ „ „
△—△ 22 „ „ „
- - - - 98 „ „ „

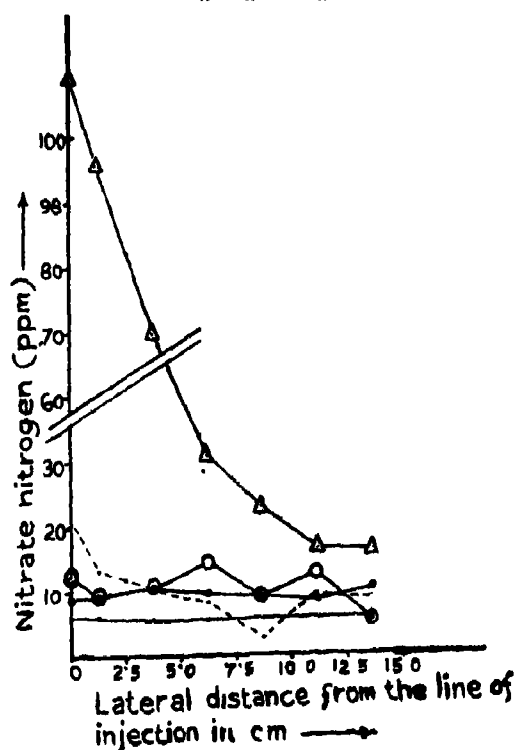


Fig. 3A. Lateral movement of nitrate nitrogen.
—— before application
●—● 2 days after application
—— 7 „ „ „
▲—▲ 22 „ „ „
- - - - 98 „ „ „

has been shown. At 2 days and 7 days after application, rate of nitrification was noticeably less in comparison to that after 22 days. After 2 days and 7days intervals the rates of nitrification were approximately 1% and 2.5% respectively. Moreover, the rate was higher at the periphery of the horizontal cylindrically shaped anhydrous ammonia retention zone This suggests a partial sterilization of the soil by anhydrous ammonia application[3,7]. Nitrification was appreciable after 22 days both laterally and vertically Fig 3A shows lateral movement of nitrate-nitrogen after 22 days upto 12.5 to 15 cm distance from the line of injection with gradual decrease This might be due to diffusion of nitrate through soil solution Fig 3 shows that vertical distribution of nitrate was not appreciable at greater depths beyond 18 cm. This is because of instability of nitrate at higher moisture condition (where partial water logging leads to reduction) This is supported by higher *p*H and moisture percentage at greater depths.

From the movement and transformation study of anhydrous ammonia in field soil the following conclusion could be drawn.

A. Movement of ammonia in soil under the experimental condition was within 3.7 cm radius from the line of injection and this was associated with a rise of *p*H. The *p*H, however, approached its original value after 22 days of application of anhydrous ammonia.

B. Transformation of added NH_3 to nitrate started from the periphery of the horizontal cylindrically shaped ammonia retention zone and it moved towards the point of injection This might be, as stated earlier, due to partial sterilization of soil microbes by free ammonia[4]

C. Estimation of nitrite nitrogen revealed no nitrite accumulation at the line of injection unlike observations reported by other workers[8-10]

D. Nitrification was negligible upto 7 days from the date of ammonia application and thereafter appreciable nitrification started

The above observations are interesting and promising for upland row crop and water logged paddy cultivation. Restricted movement of ammonia suggests a possibility of using anhydrous ammonia as side dresser without appreciable root damage to standing crop or germination of sown seed Secondly, the initially slow nitrification of added NH_3 suggests a way out for preplanting application of anhydrous ammonia in dry field and subsequent incorporation of water for irrigation within 7 days without appreciable loss of added nitrogen through leaching of nitrate. Thereafter the nitrification is fairly rapid so as to support the initial growth of the tender plants as well as the standing crop Hence the possibility of the use of anhydrous ammonia as a fertilizer seems to be promising

Some doubts from time to time that exsist about proper use of anhydrous ammonia are due to probable high volatilisation loss under high atmospheric temperature prevailing in India and small land holding coupled with poor level of farm mechanisation. But these are not fully convincing While volatilisation loss can be checked considerably by adopting proper agronomic practices and manipulating the application technique, small ammonia applicators can easily be operated on Custom Hire-Service in agriculturally developed areas of Punjab, Haryana, Uttar Pradesh, Maharashtra, Tamilnadu, Andhra Pradesh and West Bengal where tractor drawn equipments are already in use.

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Role of Phosphate and Organic Matter in the Management of Lateritic Soils for Increasing Productivity

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Laterites and lateritic soils occupy large areas in the states of West Bengal, Bihar and Orissa. The pH of these soils range from 5.0 to 6.5 or even less. They are poor in calcium, organic matter, available phosphate and exchangeable bases. Due to poor return many of these have gone out of cultivation and hence their proper management for increasing crop production has a vital bearing on the agricultural economy of the respective states.

The utility of phosphates in crop production, when mixed with decomposing organic matter has been advocated. As such, a large number of field trials were conducted extending for over 3 to 10 years in the lateritic soils of West Bengal with phosphate and organic matter. It has been found that a mixture of all kinds of organic matter along with phosphatic fertilizers is best suited for the management of lateritic soils by enriching the soil nitrogen, decreasing their acidity, saving the leaching away of lime and supplying available phosphate and calcium.

NEXT to nitrogen, phosphorus is one of the most essential nutrient required for proper plant growth. In all chemical and biochemical reactions taking place in soil, phosphates present, or added play an important role in maintaining soil productivity. Phosphates have got real value in crop production when these are mixed with decomposing organic matter since their use stimulates the nitrogen fixing bacteria, both symbiotic and non-symbiotic to greater activity[1,2]. In our country, the supply of phosphatic fertilizers has been mainly in the form of bone meal. Basic slag, a bye-product of steel industry, is also a source of phosphate but the total and available phosphate of the indigenous product is low. Large deposits of rock phosphates have also been found in our country.

Indian soils show considerable variation in their physical, chemical and microbial character due to widely diverse parent materials, topography and climatic conditions. Good results have been obtained when phosphate along with decomposing organic matter has been used than using either of them alone.

An attempt has been made in this paper to discuss the physico-chemical role of phosphatic fertilizers and organic matter in the management of lateritic soils for increasing crop production.

Characteristic of lateritic soils :

Laterites and lateritic soils of tropics have developed on rocks of very ancient origin. These are weathered due to high temperature and intermittent dry and moist climate. The land of these places is usually undulating and soil erosion has taken place. Iron concretions are dispersed on the surface and honey comb vesicular structured lateritic beds containing oxides and hydroxides of iron and aluminium are present in the subsurface region of the profile. Iron and aluminium rich clay sometimes hardens to different degree of hardness due to dehydration caused by high temperature with intermittent dry and wet climate. In West Bengal laterite and lateritic soils occur in the districts of Birbhum, Bankura, Midnapore and parts of Burdwan.

Laterite and lateritic soils are light textured and porous. Due to leaching of bases they are acidic in nature (pH ranges from 5.0 to 6.5 or even less) and are poor in calcium, organic matter, available phosphate and exchangeable bases. Kaolinite is the predominent clay mineral of such soils having exchange capacity of the order of 3 to 12 me/100 g of soil. Due to poor return, many of these soils have gone out of cultivation and hence proper management of these soils for increasing productivity has a vital bearing on the agricultural economy of the respective states where these soils occupy large areas.

Physical and chemical compositions of some typical lateritic soils of West Bengal are presented in Table 1. Some field experiments were carried out for a number of years using phosphatic fertilizers (both water soluble and water insoluble) with and without organic matter specially in laterite and lateritic soil regions of West Bengal in order to find out sustained effect of these treatments on crop yield.

Effect of phosphatic fertilizer (water soluble) mixed with decomposing organic matter :

In lateritic soil regions of Midnapore and Suri (Birbhum) in West Bengal superphosphate was applied with and without organic matter (wheat straw, cow dung and water hyacinth) and the yield

TABLE 1—MECHANICAL AND CHEMICAL ANALYSIS OF SOIL SAMPLES (PERCENTAGE ON OVEN DRY BASIS)

	Suri (Birbhum) (lateritic sandy loam)	Midnapore (Laterite)
Coarse sand	30 14	12 56
Fine sand	32.06	28.32
Silt	20.02	35.80
Clay	18.06	23.34
Fe_2O_3	4.06	1.94
Al_2O_3	5.42	3.98
CaO	0 27	0 15
P_2O_5	0 05	0.04
Ex. Ca (% me)	4.38	3.18
Total bases (% me)	12.05	4.15
Total-C	0.35	0.26
Total-N	0.06	0.04
*p*H	5.7	5.8

TABLE 2—AVERAGE YIELD OF PADDY GRAIN IN Q/ha

Treatment	Midnapore		Suri (Birbhum)	
	Paddy yield	% increase in yield over control	Paddy yield	% increase in yield over control
1. No manure	12.7	—	14 4	—
2. Organic matter (12 5 tonne/ha)	16 4	29 1	18 3	27 0
3 Super phosphate (50 kg P_2O_5/ha)	13 8	8.7	15 6	8 3
4. Organic matter + superphosphate (2+3)	16 8	32 2	18 9	31.3

of paddy was recorded year after year. The experiment was continued for 3 years. The average results obtained are given in Table 2

Similar results were obtained in another lateritic soil region at Sriniketan (Birbhum) after continuing the experiment for 6 years by the application of 33.7 kg and 67 4 kg P_2O_5 per ha in the form of superphosphate in combination with 10 tonnes per ha of farm yard manure (see Table 3)

TABLE 3—AVERAGE YIELD OF PADDY GRAIN IN Q/ha

Treatment	Paddy yield	% increase in yield over control
1. Control	15 6	—
2. 33.7 kg P_2O_5/ha	23.5	50.6
3. 67.4 kg P_2O_5/ha	24 1	54.5
4. 10 tonne F.Y M./ha	18.9	21 2
5. 33 7 kg P_2O_5 + 10 tonne F.Y M.(2+4)	25.8	65 4
6. 67 4 kg P_2O_5 + 10 tonne F.Y.M.(3+4)	27 2	74.4

After the end of the above two experiments physical and chemical analysis of the soils of experimental plots were carried out. Marked improvements in the physico-chemical properties of these soils were observed. It, therefore, shows that application of water-soluble superphosphate either alone or in combination with organic matter/ F.Y.M. not only increases the crop yield but also results in an improvement in the physico-chemical properties of the soil.

Effect of phosphatic fertilizer (water insoluble) mixed with decomposing organic matter :

Experiment was conducted at lateritic soil region, Suri (Birbum), with water insoluble phosphatic fertilizers like bone meal in combination with and without application of farm yard manure. The experiment was conducted for 12 years. The results are given in Table 4.

TABLE 4—AVERAGE YIELD OF PADDY GRAIN IN Q/ha

Treatment	Paddy yield	% increase in yield over control
1. Control	23.6	—
2. 22.4 kg P_2O_5/ha	25.6	8.5
3. 44.8 kg P_2O_5/ha	25.9	9.7
4. 10 tonne F.Y.M./ha	28.5	20.8
5. 22 4 kg P_2O_5 + 10 tonne F.Y.M. (2+4)	30.5	29.2
6. 44 8 kg P_2O_5 + 10 tonne F Y.M. (3+4)	34.3	45.4

In this case also marked improvement in the physico-chemical properties of the soil was observed after 12th year of the experiment. It is therefore concluded that in lateritic soil, application of water insoluble phosphates like bone meal, which is mainly tricalcium phosphate, either alone or in combination with farm yard manure can increase the crop productivity and at the same time improve the physico-chemical properties of such soils.

Effect of phosphate on the loss of lime by leaching :

Lateritic soils contain much less exchangeable calcium in the exchange complex. Hence attempt should be made to prevent loss of lime due to leaching from these soils and decrease their lime requirement for increasing productivity. Burgess[8] reported decrease in lime requirement of soil and increase in crop yield by the application of both water soluble phosphate (superphosphate) and water insoluble phosphates (rock phosphate, ground bone, thomas slag etc.). Treating lateritic acid soils by rock phosphate or bone meal containing calcium and phosphate is always better than by the application of calcium carbonate. This is due to the fact that the solubility of $CaHPO_4$, which is formed in sufficient quantity on the addition of rock phosphate or bone meal to these types of soils, is less than $Ca(HCO_3)_2$ formed on the addition of $CaCO_3$. Hence leaching of calcium compounds from such soil is certainly less than when $Ca_3(PO_4)_2$ is added to soil instead of $CaCO_3$. Moreover, both calcium and phosphate ions are made available from rock phosphate or bone meal while from $CaCO_3$ only calcium is made available.

Residual effect of phosphates :

Residual effect of superphosphate has been studied in lateritic soil region at Sriniketan (W. Bengal). Superphosphate was applied continuously for five years and the residual effect was noted in the sixth year. The results are recorded in Table 5. These results clearly indicate that application of

phosphatic fertilizers in lateritic soils has also residual effect which is beneficial for the suceeding crop. Hence it can be inferred that the fertility of soils is sustained specially by the use of phosphatic materials.

TABLE 5—INCREASE IN YIELD OF PADDY GRAIN OVER CONTROL IN Q/ha

Loction	Doses of phosphate	
	33 7 kg P_2O_5/ha	67 4 kg P_2O_5/ha
Sriniketan (Lateritic soil)	+2 48	+1 11

Effect of phosphate and organic matter on the fixation and loss of nitrogen from soils :

Ghosh[4] reported marked increase in the nitrogen content of soil when organic material like starch undergoes slow oxidation in presence of phosphate Similar results were also obtained by Dhar and coworkers[5] by using straw, water hyacinth, coal etc, as organic matter and phosphate. These authors[5] further reported retardation of the loss of nitrogen when ammonium sulphate was applied to soil along with phosphate

The observations recorded here, some extending for more than 10 years, clearly reveal that phosphatic fertilizers (both water soluble and water insoluble) like superphosphate, bone meal, rock phosphate, basic slag etc. in presence of decomposing organic substances in lateritic soils can enrich the nitrogen content of these soils, decrease their lime requirement and also leave residual effect for the next crop

From all these considerations it can be concluded that a mixture of various kinds of organic matter along with phosphatic materials is best suited for the management of lateritic soils by enriching the soil nitrogen, decreasing their acidity, saving the leaching away of lime and supplying available phosphate, calcium and trace elements for increasing plant growth. In general, for getting maximum benefit for water insoluble phosphate fertilizers, it is desirable to incorporate these materials along with organic matter 1½ to 2 months before the sowing of crop so as to mix them well with lateritic acid soils while for water soluble single, double or triple superphosphate it is preferable to place these fertilizers preventing as far as possible to mix with the existing soil so that they can be quickly taken up by crops and are not fixed in soil It is, therefore, evident that application of a mixture of phosphatic fertilizers and organic matter play a big role in the management of lateritic soils and this should be advocated for increasing crop production and maintaining fertility of these soils

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Thermoosmosis in Membranes

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The theories proposed to interpret the process of thermoosmosis (chiefly of liquids) in membranes have been critically examined. The limitations of the thermodynamic approach have been pointed out, and the scope of the radiation pressure theory (originally proposed to deal with thermoosmosis of macromolecular solutions) in coupled transport processes discussed The significance of membrane-water interactions has been highlighted in terms of the phenomenon of epitaxis The discrepancies existing in the experimental results are attributed to the neglect in the classical theories of the membrane factor. The review is concluded with a mention of the possible role of thermoosmosis in living systems

WHEN a temperature gradient is imposed across a membrane separating two adjacent portions of a fluid or in general, a multicomponent solution, each of which is uniform by itself, the flow of thermal energy induces a mass flow through the membrane by way of coupling Such migrations are referred to as "thermoosmosis"

Lippman[1] and Aubert[2] first reported appreciable thermoosmosis of water and electrolyte solutions through a number of membranes. They considered the thermoosmosis of electrolytes across charged membranes as a electrochemical phenomenon and related to electroosmosis This view was later supported by Sollner and his co-workers[3] The work of Ernst and Koczkas[4,5] was criticised by Ursprung[6] and need not be considered here Derjaguin and Sidorenkov[7] reported results on thermoosmosis of water and other liquids through sintered glass filters. These experiments were repeated (and expanded) by Denbigh *et al*[8], who concluded that much of the previously reported effect was due to thermal expansion. Further, they were of the opinion that the sure cases of thermoosmosis involved some electrokinetic mechanism and can not be explained on the basis of classical thermodynamics

Denbigh and co workers also studied the thermoosmotic flow of various gases through rubber membranes[9]. Similar studies, using different membranes, were conducted by Mason *et al*[10,11,12,13], Hanby[14,15,16], Rastogi *et al*[17], and others.

Meanwhile, Haase[18-23] performed thermoosmotic experiments with pure liquids, and solutions of non-electrolytes and presented theoretical considerations. Similar studies involving liquid systems were conducted by Rastogi and Singh[24], Dariel and Kedem[25], and more recently by Gaeta and Mita[26-29], who worked with solutions of macromolecules and developed the "radiation pressure theory" to account for their results.

Whereas the diffusion of gases through porou membranes under the influence of a temperatur gradient has been extensively studied and i amenable to the existing theoretical treatments, th corresponding phenomenon with liquids is a subjec of controversy at both theoretical and experimenta levels An agreement between theoretical predic tions and experimental results is also lacking i some cases This has been appropriately expresse by Haase[18] who maintained that only a few, an in part questionable, observations on thermoosmosi in liquid systems were extant. In the present review therefore, thermoosmotic experiments conducted and results obtained with liquids will be examined mainly with only a passing reference to the experiments involving gases, a field more exact, and thoroughly discussed as compared to the situation with liquids

Theories of thermoosmosis

It is accepted that the membrane in thermoosmosis experiments acts as a seat of the phenomenon of thermal diffusion and therefore, theories proposed to deal with the latter, have been considered in connection with thermoosmosis too Such theories, by their very nature, pay scant attention to the nature of the membrane and the interaction of the latter with the diffusing substance, and obviously this constitutes the greatest lacuna of these theories. The "radiation pressure" theory makes an attempt to take into consideration the specific membrane interactions

Although the process of thermal diffusion in condensed phases ("Soret effect") has been studied for many years and several theories, starting with van't Hoff's osmotic pressure theory[30], have been put forward from time to time, the situation is still far from well understood. Most of these earlier theories, which include some rather involved kinetic theories due to Wirtz and Hiby[31], Alexander[32],

Denbigh[33], Drickamer[34] and others will be skipped off (these theories are reviewed by Sanyal[35]) and we shall refer to the most general theory dealing with such non-isothermal transport processes, namely the non equilibrium thermodynamic theory, based on Onsager's Reciprocity Relations (O.R.R.). In a simple treatment of this theory, all gradients in temperature and chemical potentials (if any) are supposed to be confined within the membrane phase (which may be attained by keeping each bulk phase thoroughly mixed). Furthermore, a state of thermodynamic equilibrium with respect to temperature and partitioning of solutes is assumed to exist between the bulk phase and the membrane at each interface. The temperature gradient across the membrane is also considered linear within the latter. It is often difficult to realise these requirements in practice, and in particular, existence of unstirred Nernst's layers in the vicinity of the membrane interfaces has been proposed[36], the net effect of which is to diffuse (and reduce) the effective temperature gradient across the membrane.

With this back-ground, we may proceed to formulate the linear phenomenological equations for flux densities through the membrane in terms of the language of irreversible thermodynamics. The treatment given follows that of Sanyal and Adhikari[37] which deals, in detail, with the essential features of the theory. The following is an extension of this theory to membrane-transport.

If J_1 and J_2 are the flux densities of heat and matter, respectively, and X_1 and X_2, the corresponding driving (thermodynamic) forces, then

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad \dots (1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \quad \dots (2)$$

Here, $J_{membrane} = 0$ defines the reference frame for J_1 and J_2. L_{11} and L_{22} are the "direct" phenomenological coefficients for the independent processes of thermal conduction (L_{11} is related to the thermal conductivity of the membrane phase) and diffusion through the membrane, while L_{12} and L_{21} are the "cross-effect" coefficients representing coupling between the two flows in the membrane phase. The fluxes and the forces are so chosen as to be linearly independent and to satisfy the following relation ;

$$\sigma \propto (J_1X_1 + J_2X_2)$$

where σ is the rate of entropy production (due to irreversible processes occurring) per unit volume of the system. The purpose of such a choice for J's and X's is to ensure the applicablity of O.R.R between the cross-effect coefficients, namely the equality,

$$L_{12} = L_{21} \quad \dots (3)$$

Relations of this type (viz. eq. 3) greatly reduce the number of independent phenomenological coefficients to be determined by experiment in any coupled transport process, and hence are advantageous.

These linear relations between J's and X's, viz. eqs. (1) and (2), are in fact the limiting cases, valid only for small values of the forces, of more general non-linear phenomenological equations. The latter depends, for their application in practical systems, on the symmetry of the matrix of higher-order phenomenological coefficients in addition to Onsager's relations[37].

For the case of thermoosmosis of a gas through a porous partition, we can define the forces as follows (ideal gas behaviour assumed) ;

$$X_1 = -\frac{1}{T} \cdot \frac{dT}{dx} \quad \dots (4)$$

$$X_2 = -\frac{RT}{p} \cdot \frac{dp}{dx} \quad \dots (5)$$

where p is the gas pressure (the gas in the bulk is supposed to be in equilibrium with the membrane interface saturated with this gas).

Evidently, when $X_1=0$, it follows from eqs. (1) and (2)

$$J_1 = L_{12}X_2 = -L_{12}\frac{RT}{p}\frac{dp}{dx} \quad \dots (6)$$

and

$$J_2 = L_{22}X_2 = -L_{22}\frac{RT}{p} \cdot \frac{dp}{dx} \quad \dots (7)$$

$$\text{Thus, } \left(\frac{J_1}{J_2}\right) X_1=0 = \frac{L_{12}}{L_{22}} ; \quad \dots (8)$$

or, $J_1 = \frac{L_{12}}{L_{22}} J_2$ under isothermal conditions.

We now introduce the heat of transport $\hat{Q}$ as the amount of heat absorbed per mole of a diffusing substance from the region it leaves and released in the region it moves into, under isothermal conditions (and with migration of no other component in a polycomponent system), i.e.,

$$\hat{Q} = \left(\frac{J_1}{J_2}\right)_{X_1=0} = \frac{L_{12}}{L_{22}} \text{ from eq (8)} \quad \dots (9)$$

A detailed discussion leading to physical insight into $\hat{Q}$ has recently been given by Sanyal and Adhikari[37].

Now, at the steady state, $J_2=0$, and by using O.R.R., viz. eq. (3), we obtain from eq (2)

$$L_{21} X_1 = -L_{22} X_2$$

$$\text{i.e., } \left(\frac{X_2}{X_1}\right)_{st} = -\frac{L_{21}}{L_{22}} = -\frac{L_{12}}{L_{22}} = -\hat{Q} \quad \dots (10)$$

(from eq. 9)

(the subscript 'st' denotes the steady state). Substituting eqs. (4) and (5) into eq (10),

$$\hat{Q} = -\frac{RT^2}{p} \cdot \frac{dp}{dT} \quad \dots (11)$$

Using $p = RT/\bar{V}$, one obtains from eq. (11)

$$\left(\frac{dp}{dT}\right)_{st} = -\frac{\hat{Q}}{\bar{V}T} \quad \dots (12)$$

where $\bar{V}$ is the molar volume of the diffusing gas, and T, the mean temperature, here $(dp/dT)_{st}$ refers to the steady state value across the membrane. A similarity between eq. (12) and the Clapeyron's equation for isothermal phase-transition in reversible thermodynamics is worth noting.

It must be emphasised at this stage that such thermoosmosis, although somewhat analogous in its microscopic aspects to the thermal effusion of gases, is clearly distinct from the latter; the effusion always leads to the higher pressure of gas on the warmer side of the membrane, while in thermoosmosis, various gases behave differently and hydrogen, in particular, accumulates on the cooler side of a rubber membrane[9]. Rastogi *et al*[17] distinguished in this context, between viscous flow of a gas through a membrane and the corresponding thermal migration by setting two limits to $\hat{Q}$ values. Thus, if λ be the mean free path of a gas molecule, and a the diameter of a typical pore in the membrane the kinetic theory predicts that,

$$\lim_{(a/\lambda)\to 0} \hat{Q} = -RT/2 \text{ (Knudsen limit)},$$

and

$$\lim_{(a/\lambda)\to \infty} \hat{Q} = 0 \text{ (Poiseuille limit)}.$$

Cases of intermediate (a/λ) values are much more complicated. In particular, there is normally some interaction between the gas and the membrane-substance which tends substantially to modify the value of the heat of transport by adding a heat of solution term to it. It is to this latter type of membrane-transport processes that the term thermoosmosis is generally applied.

One has to turn to the kinetic theory, however, in order to assign physical meaning to the first order (and higher order) phenomenological coefficients. Denbigh and Raumann[9] first developed such a theory for the transient approach to the steady state, which was later generalised by Crowe[38] to cases of differing and changing gas volumes. More recently, Mason and Evans[10-13] have advanced the "dusty model", a general theoretical approach in which the porous medium is visualised as a collection of stationary "dust" particles.

It is worth emphasising here that the choice of the thermodynamic forces X_1 and X_2 is not arbitrary and it needs to be pointed out that some authors have erroneously defined temperature and pressure differences across the membrane as forces, instead of the corresponding gradients.

In the following sections, experimental results, obtained by various workers, will be introduced and the reasons for discrepancies will be discussed.

Experiments on thermoosmosis of gases :

Although the treatment of the previous section is generally adequate for interpreting the results of thermoosmotic experiments with gases, discrepancies were noted between $\hat{Q}$, obtained from the steady state equation, viz. eq. (12), and those determined from isothermal and thermoosmotic permeabilities[14,15]. Introduction of the second-order phenomenological coefficients does sometimes lead to better agreements. According to Hanley and Steele[15,16], the difference between the "true" $\hat{Q}$ and the steady state value of $\hat{Q}$ passes through a maximum at $(a/\lambda) \simeq 0.2$, and tends to small values for $(a/\lambda) < 0.9$.

Conflicting values of $\hat{Q}$ have sometimes been recorded by various workers. Thus, Rastogi[17] reports 62.77 cal. mol^{-1} (the mean temperature T_m used=327 K) as $\hat{Q}$ for thermoosmosis of CO_2 through unglazed porcelain, while Denbigh and Raumann[9] obtained a value of 1860 cal. mol^{-1} (T_m=304.3 K), and Bearman[39,40] got 980 cal. mol^{-1} (T_m=318 K). Further, Rastogi observed no dependence of $\hat{Q}$ on the mean temperature of the experiment, in total conflict with eq. (12).

Experiments on thermoosmosis of liquids :

As briefly mentioned earlier, Haase[18-22] and co-workers conducted extensive studies on thermoosmosis of water through cellophane 300 and 600 membranes. More recently, they have extended their study to methanol-cellophane systems.

In his experiments with cellophane 600 membranes, Haase[23] reports an almost linear dependence of $\hat{Q}$ on T_m over a wide range of mean temperatures (10° to 90°) with $\hat{Q}$ being a monotone-decreasing function of T_m and its sign reversing at 55° to 60°. Such a linear variation of $\hat{Q}$ with T_m over a wide range of temperatures is unexpected since the phenomenological coefficients are unlikely to remain linear in that range. As for the conflicting results, Rastogi and Singh[24], who also studied thermoosmosis through cellophane membranes, reports a $\hat{Q}$ equal to 0.120 cal mol^{-1} at T_m=46° for water across cellophane while Haase[22] finds 0.535 cal. mol^{-1} at T_m=45.42. At T_m=50°, Rastogi observed $\hat{Q}$=0.090 cal. mol^{-1}, while the corresponding value reported by Haase is 0.240 cal. mol^{-1} at T_m=50.84°. Finally, at T_m=54°, Rastogi's value for $\hat{Q}$ is 0.130 cal. mol^{-1} whereas that of Haase is 0.0178 cal. mol^{-1} at T_m=55.51°.

As one moves on to methanol-cellophane system, the situation becomes even worse. Thus, Rastogi[24] obtains the value of $\hat{Q}$=+1.33 cal. mol^{-1} at T_m=42° as against Haase's[23] −0.885 cal. mol^{-1} at T_m=43.77°. In fact, Haase reports negative $\hat{Q}$ values

for all the mean temperatures from 9.32° to 59.15°. Both these authors appear to have defined their thermodynamic forces erroneously in that ΔP and ΔT (which they consider as forces) are not true "gradients".

In their study of thermoosmosis in the presence, as well as absence, of an osmotic pressure difference, using cellulose acetate membranes, with aqueous sodium chloride and pure water on the hot and the cold side, respectively, Daniel and Kedem[25] report enormously high values of $\hat{Q}$ for water. At 25°, they obtained $\hat{Q}=390$ cal. mol^{-1} compared to Haase's[21] 1.72 cal. mol^{-1} at $T_m=25.33°$ At 45°, they get 440 cal. mol^{-1}, while Haase obtains 0.535 cal. mol^{-1} for $T_m=45.42°$, and Rastogi reports 0.120 cal. mol^{-1} at 46°. Furthermore, Daniel and Kedem's heat of transport is an increasing function of temperature, T_m, while Haase's $\hat{Q}$ decreases with T_m It is noteworthy that both Hasse and Rastogi appear to have neglected the temperature drops in their solutions, whereas Daniel and Kedem have made an allowance for such lowering of temperature.

Thermoosmosis of macromolecular solutions : Radiation pressure theory :

In recent years, Gaeta and his associates[26-29], have developed the "radiation pressure theory" to account for the thermodiffusive phenomena in condensed phases. Based on the original idea of Debye[41] that the thermal energy in liquids can be represented as an ensemble of elastic longitudinal waves of very high frequency ("Debye waves"), this theory proposes that the flow of heat in liquids produces a flux of mechanical momentum which is proportional to the "momentum conductivity" of the fluid. The latter is the ratio of thermal conductivity to the velocity of elastic waves (sound waves) in the medium itself. Consequently, the continuous flow of these "thermal waves" from the hot to the cold side in a non-isothermal solution results in a force that acts on the dissolved (or, suspended) particles in the absence of convection The direction of this force is parallel to the temperature gradient, and its magnitude is given by[26]

$$F=2\tau^2_{l,p}\left(\frac{k_l}{v_l}-\frac{k_p}{v_p}\right)\sigma'\frac{dT}{dx} \quad \dots (13)$$

where $\tau_{l,p}$ is the characteristic coefficient of transmission of elastic waves from the liquid to the material the particles are made of; k_l, v_l and k_p, v_p are the thermal conductivity and velocity of sound in the liquid and in the particles, respectively, (obviously, k/v is taken as the momentum conductivity) ; σ' is the cross sectional surface area of a given particle and (dT/dx), is the temperature gradient. The sign of the force F, and consequently, the direction of migration of the solute, depends upon the sign of the expression,

$$\left(\frac{k_l}{v_l}-\frac{k_p}{v_p}\right) \quad \dots (14)$$

Gaeta[27] further obtained a relation between the Soret coefficient S[38] and the molecular weight M of the solute as

$$S=HM^{2/3} \quad \dots (15)$$

where H is a constant dependent on the geometry and the density of the solute particles.

According to this theory, thermal diffusion is a consequence of a mechanical interaction of thermal elastic waves with matter.

Gaeta and co-workers have applied the radiation-pressure approach to a number of systems, mostly solutions of high molecular weight biologically important compounds with considerable success. However, in view of the lack of data on the values of k and/or v, in various solvents and solute materials, it does not seem possible at present to fully evaluate the validity of this approach. Moreover, the macroscopic nature of the quantities k and v adds another difficulty to the direct application of the theory to solutions of molecular, rather than macromolecular particles.

Recently, Gaeta and Mita[29] have extended the radiation-pressure theory to thermoosmosis (which they have named "thermodialysis") of liquids. In particular, they have stressed the importance of "epitaxis", the adsorption of solvent molecules on the pore-walls of the thermoosmotic membrane, leading to the formation of thin layers of sorbed solvent with physicochemical properties, very diffierent from those of the bulk solvent in the larger pores of the membrane Depending on the nature and magnitude of the solvent-membrane interaction, the sign of the expression,

$$\left[\left(\frac{k}{v}\right)_{l^*}\left(\frac{dT}{dx}\right)_{l^*}-\left(\frac{k}{v}\right)_p\left(\frac{dT}{dx}\right)_p\right] \quad (16)$$

where l^* stands for the "epitaxed liquid" will be positive, or negative, and consequently, the solute particles will migrate to the cold, or hot side of the membrane, respectively. In this way, they have been able to account for the direction of solute flow in a number of systems, and have provided an explanation for the reversal of flow of polyvinyl polymers (in 1-butanol solvent) across nucleopore membranes of gradually decreasing pore-size so that the effect of epitaxis (i.e., of eq. 16) also becomes progressively more important.

Discussion

a) *Sources of error :* It does not appear quite simple to locate the possible sources of error which have caused such enormous discrepancies between the results of different investigators. In some cases, however, much could have been desired to ensure better experimental arrangements. Thus, in one particular case[17], no thermostat was used to regulate the temperature of each compartment containing the diffusing gas. In the thermoosmosis of liquids, some error appears inevitable while measuring the

amount of flow and the hydrostatic pressure difference through the use of capillaries which protrude out of the thermostated region, and are therefore exposed to the temperature fluctuations of the atmosphere. Moreover, it is difficult to allow for the differential thermal expansion in such non-isothermal experiments while monitoring the movement of the liquid meniscus in exposed capillaries unless the temperature of the liquid in the capillaries are known precisely.

Another problem is the presence of unstirred layers and the difficulty in maintaining a uniform temperature in the proximity of the membrane, even under conditions of vigorous stirring[42].

Perhaps the most important of all the considerations, but much neglected to date, is the overwhelming dependence of the phenomenon on the nature of the membrane. Not only the membrane alters the magnitude of the effect, but it can even change its direction[29].

(b) *Importance of epitaxis* : While discussing the significance of the "membrane factor", the phenomenon of epitaxis in the membrane should be given due consideration. The latter has been shown to be a dominant factor in membrane-transport processes in some biological systems as well[43-45]. Doubtless, the structure of the membrane and consequently the nature of its interaction with the diffusing species, are the determining factors of any membrane transport process, although the irreversible thermodynamic theory, discussed earlier can not provide any information of this kind, for the dependence of the phenomenological coefficients on the membrane-solution system is not specified.

There is strong evidence indicating the existence of expitaxed liquid and, in particular, "structured water" in hydrophilic membranes. Ordered water in living body was first reported by Cape[44] in rat muscles and brain through the use of nmr line broadening techniques. By similar means, Hazlewood *et al*[43] reported the existence of two types of ordered water in skeletal muscle. Recently, Froix and Goedda have studied the interaction of water with cellulose membrane[46] and the effect of temperature on this interaction[47], by means of nmr relaxation times. They have detected a drastic change in molecular mobility at the point of plasticization, which is characterised by the adsorption on the primary sites. They have further detected two types of water in the cellulose-water system : "bound" water and "free" water. The physical properties of both were changed drastically and the freezing point of bound water was found to be lowered to 196 K, and that of free water to between 221 K and 252 K.

Interaction of water wtih cellulose acetate membranes has also been studied, by, among other techniques, nmr and differential scanning calorimetry[48-50], and the results indicate the presence of "unfrozen" but somewhat immobilised water in such membranes. Such "less mobile" water need not be "ice-like" in structure as has been reported by recent infra-red studies on the state of water in cellulose acetate membranes by Toprak *et al*[51]. These workers have accounted for the observed salt-rejection by cellulose acetate membranes in reverse osmosis in terms of a low degree of association of water in contact with the membrane. The latter leads to a dissimilarity in the intermolecular structure and hydrogen bond strength of water molecules in cellulose acetate with those in the liquid water and this is proposed to be responsible for salt-exclusion.

In any event, what emerges is that the state of water, sorbed in various natural and synthetic polymer membranes is very different (whether weaker or stronger hydrogen-bonded than in pure liquid water) from that of liquid water.

(c) *Scope of radiation pressure theory* : In view of the interesting physico-chemical aspects of thermal diffusion and thermoosmosis as well as their apparent relevance in biology and other disciplines, the need of a more detailed and unified theoretical approach seems obvious In this regard, the radiation pressure theory of Gaeta *et al* appears to be promising. It is generally thought that the thermal waves of liquids have frequencies of the order 10^{0} to 10^{13} Hz. If their velocity of propagation in water is taken as 1500 m sec^{-1}, a simple calculation reveals that wavelengths, as short as several Å, are to be expected. This is certainly within macromolecular and perhaps even molecular dimensions and so the interaction between such thermal waves and solute particles seems plausible.

Before we conclude, mention must be made of the probable role thermoosmosis is expected to play in determining the membrane selectivities in solute transport and semipermeability of various cell membranes in living systems Although the heat generated by various local metabolic changes is usually small, and may be dissipated before creating any effective temperature difference (for any appreciable period of time) between the two sides of a cell membrane, the actual temperature gradients across such membranes may be quite large in view of the extreme thinness of membranes in living systems. And, it is this temperature gradient which is the driving force for thermoosmotic flow. Some interesting work in this direction is being carried out by Gaeta and his school[30,52]. They claim to have explained the hypothesis of "sodium-potassium pump" in living systems on the basis of the radiation pressure theory they have advanced. However, it appears that much more remains to be done to this goal before anything, one way or the other, can be said with confidence.

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Phosphate Fertilization in Alluvial Soils of Allahabad Division. Interrelation in Water Soluble P, Adsorbed P and Olsen's P

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Fifteen alluvial soils of varying fertility levels selected from 5 districts of Allahabad Division were equilibrated with 0-20 ppm of P depending upon the fertility level and amounts of P in solution (W.S.P.) and in the sorbed state were determined after incubation periods of 24 hr and 30 days.

The soils of Allahabad and Fatehpur districts were found to be of high P fixing capacity and remaining districts of low fixing capacity category The ability of the soil to retain or release P varied considerably. Usually low fertility soils have also low initial water soluble P but have high P fixing capacity Soils with very low, low and high P fixing capacities alone will require high P application and there is hardly any danger of uneconomical return, whereas soils of high fertility status need little or no P fertilization In soils of high fertility category, P in the supernatant liquid was more than 0 2 or 0 3 ppm even after incubation period of 30 days.

PHOSPHATE concentration in soil solution offers an easily determined index of phosphate availability Only a small part of the total P present in soils is in the available form and, thus, an extremely small amount of P (often less then 0 1 ppm) is present in soil solution. According to Fried and Shapiro[1], P concentration in soil solution ranges from 0 001 mole/litre $\times 10^{-3}$ with average of 0 007 $\times 10^{-3}$ in acid soils to 0 03 $\times 10^{-3}$ in calcareous soils According to Russell[2] a concentration of $10^{-5}M$ phosphate (0 3 ppm) in soil solution is optimum, $10^{-3}M$ has been regarded as high and $10^{-7}M$ as low concentration. Beckwith[3] has suggested 0.2 ppm P in solution as a standard for comparative purposes because it was a reasonable value for a number of plant species Fox and Kamprath[4] obtained 95% of maximum yield when P in the solution was adjusted to 0 2 ppm.

Singh *et al*[5] found a good correlation between phosphate sorbed value and crop yields at a standard equilibrium concentration of 0.3 ppm Silva and Fox[6] obtained 92 to 99% maximum yield when P concentration in soil solution was adjusted to 0 2 ppm Ozanne and Shaw[7] in their preliminary studies, showed that equilibrium concentration of 0 3 ppm P in soil suspension was the most suitable for optimum crop yields.

Thus, a knowledge of P adsorption characteristics appears to be important in making rational statements about P avilability and phosphate fertilizer requirements. With this object in view, alluvial soils of Allahabad Division of varying fertility levels were equilibrated with P solution of known concentration and the amount of P in liquid phase was determined. An interrelation between soluble P, adsorbed P and Olsen's P was worked out.

Experimental

Soils selected. The soil samples for the present study were collected from alluvial soils of Allahabad Division comprising districts of Allahabad, Fatehpur Kanpur, Farrukhabad and Etawah. The samples were collected in such a way that soils of varying fertility categories could be obtained. General appearance of the soils, cropping pattern and previous soil test data served as a guide in collection of the samples from different fertility categories In all 40 samples (8 samples from each district) were collected and brought to the laboratory for screening for a detailed study. From amongst the samples tested for screening, 15 samples (3 samples from each district) were finally chosen for detailed study The soil samples were characterised into five fertility categories, viz. very low, low, medium, medium-high and high. The fertility-wise distribution of the soil samples chosen for detailed study was as follows : very low (3), low (2), medium (3), medium-high (2) and high (5) (figures in parenthesis denote number of samples of each category).

1 0 g soil was taken in a 100 ml conical flask. The soil : solution ratio was fixed at 1 : 20. The concentration of P added (as KH_2PO_4) varied from 0 to 20.0 ppm P depending upon fertility level of the soil. Lower concentrations were purposely added to P-rich soils. The initial concentration for each

soil was so chosen as to give final equilibrium concentration of P in the range of 0.1 to 1.0 ppm P. Few drops of toluene were added to supress the microbial action during the above reaction and the flasks were corked The samples were incubated for 24 hr and for 30 days. A 7 hourly hand-mixing in case of the former and weekly mixing for the latter was done.

After the lapse of incubation periods, the suspension was centrifuged for 20 min at 2400 rpm, supernatant liquid was separated using Whatman filter paper No. 40 and the solution analysed for P content by molybdenum blue method[8] using sulphomolybdic acid reagent. The above estimated values of phosphorus (W S P.) when subtracted from the amount of P added to the soils gave the values of P sorbed by the soils. Olsen's P was determined by the procedure of Olsen *et al*[9].

Results

Comparative data of Olsen's P, adsorbed P, W.S.P., and P in the supernatant liquid at two incubation periods is presented in Table 1 Analysis of the results shows that P adsorption is gradual and a steady state is obtained only after a prolonged contact. 80-90% of added P disappeared from solution in very-low, low and medium fertility soils with few exceptions after incubation period of 30 days.

When the incubation period is small the soils of Allahabad district and its adjoining District Fatehpur behave alike towards added P and hence can be grouped under one category while the soils from Kanpur, Farrukhabad and Etawah districts in another category The soils of the former category seem to possess high P fixing capacity and fixation of P takes place even when the soil contains as high as 24.8 ppm Olsen's P. The soils of the latter category show low P retention and a desorption is noticed in soils having Olsen's P as low as 4 0 ppm In general, the soils with higher content of Olsen's P showed sign of desorption even at low dose of P application These soils contain W S P ranging from 41 to 78% of Olsen's P.

P in the supernatant liquid is found to be low in soils of high P-fixing capacity and values obtained are generally below the standard value of 0 2 –0 3 ppm in the untreated soils The soils of Allahabad and Fatehpur districts have a high P-fixing capacity Therefore, P in the supernatant liquid even in medium to medium-high group soils seldom exceeds the standard value. Addition of P to the soils of Allahabab and Fatehpur districts at 4 ppm and 10 ppm failed to raise the level of P in the liquid phase beyond the said limit. On further raising the level of P application, P in the supernatant went beyond 0.2 ppm P. On the other hand, soils with low fixing capacities keep more than 0.2 ppm P in the supernatant liquid and when P is added at the rate of 4 ppm the level of P in supernatant liquid shot beyond 0.2 ppm. The soils of medium to high fertility status of these districts contained invariably higher concentration of P than the specified limit The range of P in the supernatant liquid in the soils of high fertility is from 0 45 to 1.91 ppm and the values for the unfertilized soils ranged from 0.45 to 1.52 ppm.

Thus, P in the supernatant liquid is directly related to Olsen's P in soils which is used as a criteria of soil category

Relationship between sorbed P and P in the supernatant liquid at 30 days incubation periods :

Sorbed P · True picture regarding the retention of P by the soils of varying fertility categories is obtained at 30 days incubation period. Based on the findings of 24 hr incubation period, we grouped the soils from the districts af Allahabad and Fatehpur under one category and the remaining districts having low fixing capacity in another category The above categorization holds good for incubation periods of 30 days also In the first category, the retention of P varied from 90 to 100% of the added P irrespective of fertility of soils whereas in the second category the sorption of P varied with district and with change in fertility levels of soils. In Farrukhabad soils, the range of P sorbed was 62 to 95% in very low fertility category and 10 to 15% in medium-high fertility category. In soils of Kanpur, the P sorbed varied from 40 to 88% in low and medium fertility category and the range of variation in Etawah soils was from 88 to 95% for very low and high fertility soils A sample (E-2) from medium fertility group of Etawah district showed abnormal behaviour and 65% to 14% desorption was noted

P in the supernatant liquid : The amount of P in the supernatant liquid in the soils of high P fixing capacity was found much below the standard value of 0.2 or 0 3 ppm on incubating soils for 30 days ; the soils of high fertility are exceptions In soils of low and medium fertility category from Kanpur and very low category of Etawah and Farrukhabad districts, the content of P in the supernatant liquid was found below the above limit But the soils of medium fertility of Etawah and medium-high category of Farrukhabad districts showed marked high P in the liquid phase. The soils of high fertility invariably registered high P content in the liquid phase even at this incubation period (30 days).

It may thus be concluded that the soils of high P fixing capacities alone will require high P application whereas soils of high fertility level need little or no P fertilization. In case of soils of other categories (very low and low), application of P even at the increased rate will not be uneconomical. The rate of P addition has to be altered to get P in the supernatant liquid at 0.3 ppm· level.

The soils of very low and low fertility status of Kanpur and Farrukhabad districts showed the sign of desorption at the former incubation but the adsorption was found at all the P levels of application on prolonged incubation. Similarly, 3 soils, out of the 4 soils where there was no sorption at 24 hr, registered sorption at the latter incubation period. It is thus clear that the soils showing no retention

TABLE 1—RELATIONSHIP BETWEEN OLSEN P, WATER SOLUBLE P AND SORBED P IN SOILS OF VARYING FERTILITY AT TWO INCUBATION PERIODS

Fertility status	Sample No.	Treatment	Olsen P (μg P/g soil)	Sorbed/desorbed P (μg P/g soils)		W.S.P. (μg P/g soil)		P in supernatants (μg P/ml)	
				24 hr	30 days	24 hr	30 days	24 hr	30 days
1	2	3	4	5	6	7	8	9	10
Very low	E-1	S	4.0	–	–	–	–	–	–
		S+W	3.0	–	–	0 8	0.4	0.04	0.02
		S+4P	5.0	3.6 (90)	3.8 (95)	1 2	0 6	0.06	0.03
		S+10P	7 0	8 0 (80)	8.8 (88)	2.8	1.6	0.14!	0.08
		S+20P	10 5	15.8 (79)	17 6 (88)	5.0	2 8	0.25	0.14
	F-1	S	1 6	–	–	–	–	–	–
		S+W	0 6	–	–	0.8	0 2	0.04	0 01
		S+4P	4 2	2.6 (65)	3 8 (95)	2.2	0.4	0.11	0.02
		S+10P	5.2	7.0 (70)	9.6 (96)	3.8	0 6	0.19]	0.03
		S+20P	11.2	10 0; (53)	19 2 (9)|	10 1	1 0	0.51	0 05
	FD-1	S	4 0	–	–	–	–	–	–
		S+W	4.5	–	–	2.8	0 4	0 14	0 02
		S+4P	5 0	0.2 (5)	3 8 (95)	6 6	0 6	0 33	0 03
		S+10P	9.0	– 2.2 (22)	9 0 (90)	15 0	1 4	0.75	0 07
		S+20P	16 0	–11.4 (58)	13 4 (67)	34.4	7 0	1.72	0.35
Low	K-1	S	6 5	–	–	–	–	–	–
		S+W	6 0	–	–	1 2	0 8	0.06	0.04
		S+4P	8.0	1.2 (30)	3 0 (75)	4.0	1.8	0.20	0.09
		S+10P	12.0	– 0 4 (4)	8 8 (88)	11.6	2 0	0.58	0.10
		S+20P	18.0	– 0 6 (3)	16.6 (83)	21 8	4.2	1.09	0 21
	K-2	S	9.5	–	–	–	–	–	–
		S+W	8.5	–	–	3.1	0 4	0.16	0 02
		S+4P	8 5	0.3 (75)	1 6 (40)	6.8	2 8	0 34	0.14
		S+10P	13 0	– 5 9 (59)	7 2 (72)	19 1	3 2	0 96	0.16
Medium	A-1	S	14 0	–	–	–	–	–	–
		S+W	9.5	–	–	1 2	0 8	0 06	0.04
		S+4P	14.0	2 4 (60)	4 0 (100)	2.8	0 8	0.14	0.04
		S+10P	16 0	5.6 (56)	9 6 (96)	5 6	1 2	0 28	0.06
	K-3	S	14 0	–	–	–	–	–	–
		S+W	10 0	–	–	2 2	1 6	0 11	0 08
		S+4P	14.0	0 1 (2 5)	3 2 (80)	6 1	2.4	0 32	0.12
		S+10P	16 5	– 6 4 (64)	8 2 (82)	18 6	3 4	0.93	0.17
	E-2	S	13 0	–	–	–	–	–	–
		S+W	12 5	–	–	8.6	7.0	0 43	0.35
		S+4P	20 0	– 4 4 (110)	2 6 (65)	17.0	8 4	0 85	0.42
		S+10P	24 0	–(148)	– (14)	33 4	18 4	1.67	0.92
Medium high	A-2	S	16 0	–	–	–	–	–	–
		S+W	10 0	–	–	1 6	0.6	0.08	0.03
		S+4P	10 0	2.8 (70)	4.0 (100)	2 8	0 6	0.14	0.03
		S+10P	11.0	8 6 (86)	9 4 (94)	3.0	1.2	0.15	0.06
	FD-2	S	18 5	–	–	–	–	–	–
		S+W	20.5	–	–	5.4	1 6	0.27	0.08
		S+4P	22.5	3.2 (80)	0 6 (15)	12 6	5.0	0.63	0.25
		S+10P	30.5	–13.8 (138)	1.0 (10)	29.2	10.6	1.46	0.53

(Continued Table 1)

Fertility status	Sample No.	Treatment	Olsen P (μg P/g soil)	Sorbed/desorbed P (μg P/g soils)		W.S.P. (μg P/g soil)		P in supernatants (μg P/ml)	
				24 hr	30 days	24 hr	30 days	24 hr	30 days
1	2	3	4	5	6	7	8	9	10
High	A-3	S	73.0	-	-	-	-	-	-
		S+W	63.0	-	-	30 4	30 70	1.52	1.51
		S+4P	60.0	- 3 8	3.2	38.2	35 0	1.91	1.75
				(95)	(80)				
	FD-3	S	38.0	-	-	-	-	-	-
		S+W	35.0	-	-	14.4	4 8	0 72	0 24
		S+4P	41.5	-15.4	- 0 4	23.8	9 2	1 19	0 46
				(385)	(10)				
	E-3	S	21.5	-	-	-	-	-	-
		S+W	16.0	-	-	12 2	7 4	0 61	0.37
		S+4P	18.5	- 1 4	3 6	17 6	7 8	0 88	0.39
				(35)	(90)				
	F-2	S	24.8	-	-	-	-	-	-
		S+W	20.4	-	-	9.0	1 6	0 45	0.08
		S+4P	26.4	1 2	3 6	11.8	2 0	0 59	0.10
				(30)	(90)				
	F-3	S	43.2	-	-	-	-	-	-
		S+W	32 0	-	-	25 2	17 4	1 26	0 87
		S+4P	38.0	- 4 0	- 1.8	33 2	23 2	1 66	1 16
				(100)	(45)				

Soil samples—A-1, A-2, A-3 From Allahabad district
K-1, K-2, K-3 From Kanpur district
E-1, E-2, E-3 From Etawah district
FD-1, FD-2, FD-3 From Farrukhabad district
F-1, F-2, F-3 From Fatehpur district

S - 1 0 g soil, W - 20 ml water, P - μg P
(Figures in the parenthesis are percentages of the added P)

at 24 hr incubation, registered gradual adsorption with increase in P application at 30 days incubation.

Discussion

When a phosphate solution is added to soils, normally a major part is retained by the soil constituents and only a small fraction of added P remains water soluble. The reaction between soil P and added P appears to continue till an equilibrium is reached Accordingly retention is likely to increase, leaving lesser amount of P in the water soluble form (W.S P).

Usually low fertility (either very low or low) soils have also a low initial water soluble P content but have high P fixing capacity. However, major part of added P gets retained by these soils, leaving only a negligible concentration of P in soil solution on prolonged contact.

However, if the soils contain high concentration of initial W.S.P, no retention of P takes place initially (first 24 hrs). These soils exhibit P retention only after an equilibrium period of 30 days

The ability of the soils to retain and release P varies considerably. The high fertility soils do not retain any P in the beginning but do so after 30 days. This indicates that P is gradually converted to insoluble P compounds. Such transformations are not unusual. Even the low fertility soils, such as Farrukhabad and Kanpur district soils which do not retain any P at the initial stage of water-logging (at 24 hrs), begin showing retention after the incubation period of 30 days.

Thus the soils of Allahabad and Fatehpur districts can be grouped together with regard to their behaviour towards P application. These soils have high P fixing capacities and as a result only a small fraction of added P remains in water soluble form. The soils of Kanpur, Farrukhabad and Etawah district with low fixing capacities can be grouped likewise separately

It can, therefore, be concluded that even increasing rates of added P to low fertility soils will not considerably contribute to W.S P whereas in high fertility soils, even the smallest dose of P (0 4 ppm P). will not be transformed into insoluble form even after 30 days This indicated that the addition of P, if needed, can be practised without any danger of fixation of P and therefore economical use of P can be envisaged.

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Post-harvest Changes in the Status of Nitrogen and Organic Carbon in Soil Treated with Fertilizers and Pesticides for Growing *Raphanus sativus*

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NH_3-N was found maximum in soils supplied with fertilizers only (C_f) and pesticides were found to inhibit the production and maintenance of NH_3-N in soils. Fertilizers and pesticides showed increased percentage of NH_3-N than the original level (OL), although natural soil showed more NO_3-N than the treated soils. In presence of metasystox there was an increase in NO_3-N percentage than the fertilizer (C_f) and carbofuran treated (P) soils. Rate of nitrification was inhibited by the presence of fertilizers and pesticides. However, pesticides increased the rate of nitrification in the soils than fertilizers only. Organic carbon percentage was found to be maximum in the original level. Pesticide treated soils had a higher organic carbon level than the fertilizers treated soil.

In modern farming uses of fertilizers and pesticides are increasing for the improvement of agricultural production. However, the addition of these chemicals cause changes in chemical and biological processes.

The effect of different fertilizers on the nitrogen and carbon cycles in the soil has been worked out[1,2,3]. Inhibition of nitrification[4-6], enhancement in N-fixation and nitrification[7], unaffected nitrification[8], nitrate accumulation[9], decline of nitrate level[10] and an enhancement in ammonical nitrogen and decline in nitrate nitrogen[11] in soil supplied with aldicarb[11] have been reported as resulting from the application of insecticides/pesticides.

Effect of pesticides on soil organic matter is not well understood, although there are reports on decline in the organic carbon level of soil[12], and adsorption of pesticides by organic matter[13].

In the present work an attempt has, therefore, been made to study these effects in detail.

Experimental

5 kg soil was taken in earthen pots and five seeds of radish (*Raphanus sativus*) were sown in each pot. One set of pots was supplied with inorganic and organic nitrogenous fertilizers alone and in combination with P and K, (C_f) at the rate of 50 : 50 : 100 kg/ha Another set of pots was supplied with the same fertilizers and carbamate insecticide (P_c) at the rate of 17.67 kg/ha. The third set of pots was supplied with fertilizers and organophosphorus insecticide (P_m) at the rate of 400 ml in 197.68 gallon/ha. Inorganic fertilizers used were ammonium sulphate (N) alone and in combination with superphosphate (P_2O_5) and muriate of potash (K_2O). Organic fertilizers used were urea (U) alone, urea in combination with inorganic P and K and cowdung manure (CM) alone. Carbamate and organophosphorus insecticides were carbofuran and metasystox, respectively.

Estimation of NH_3-N, NO_3-N and organic carbon : For the estimation of NH_3-N and NO_3-N the reported method of De[14] was used. Organic carbon of the soil was done by chromic acid colorimetric method of Dutta *et al*[15] and percentage of organic matter was calculated by multiplying the percentage of organic carbon with 1.724. The whole experiment was done in three replicates.

Results and Discussion

From the data presented in Tables 1(a), (b) and (c), it is clear that in presence of carbofuran there was more nitrate utilization by radish than in presence of fertilizers or metasystox, although the rate of nitrification was greater in presence of metasystox than carbofuran. It is quite clear that metasystox, being a sulphur containing compound, could not be broken down microbiologically so easily on the surface of the leaves and probably choked the absorbing cells of radish leaves, thereby hampering CO_2 assimilation and synthesis of glucose. Due to this adverse effect in the process of photosynthesis, the metabolic activities within the plant leaves swayed in a fashion that affected nitrate absorption/utilization for the synthesis of protein and other nitrogenous compounds. This was probably not the case with carbofuran, whose metabolic pathway in plants, insects and mammals was known to show the formation and absorption of additional energy material (O-glucose) resulting in more utilization and absorption of NO_3-N. Inspite of this result with respect to carbofuran, the residual soil treated with this insecticide showed more NH_3-N. This seems to be a microbial effect in the soil in which the additional glucose as a result of

TABLE 1(a)—POST-HARVEST CHANGES IN THE STATUS OF NH_3-N, NO_3-N, NO_3/NH_3 AND ORGANIC CARBON IN SOIL TREATED WITH FERTILIZERS AND PESTICIDES FOR GROWING *Raphanus sativus*

Changes in NH_3-N, NO_3-N, NO_3/NH_3 and organic carbon in soil.

	C_f					P_m					P_c				
Treatment	NH_3-N %	NO_3-N %	NO_3/NH_3	Organic carbon %	Organic matter %	NH_3-N %	NO_3-N %	NO_3/NH_3	Organic carbon %	Organic matter %	NH_3-N %	NO_3-N %	NO_3/NH_3	Organic carbon %	Organic matter %
Control	0.0084	0.0070	0.83	0.78	1.34	0.0042	0.0056	1.33	0 84	1 45	0 0070	0 0070	1 00	0.86	1.48
N	0 0070	0.0056	0.80	0.86	1.48	0.0070	0.0070	1.00	0.92	1 59	0 0056	0 0056	1.00	1 13	1.95
NPK	0.0070	0 0070	1.00	1.39	2 40	0 0070	0 0084	1 20	1 05	1 81	0 0070	0 0070	1 00	1.30	2 24
U	0.0070	0 0056	0 80	1 32	2.28	0.0084	0.0070	0 83	1 34	2 31	0.0084	0 0056	0 67	1 53	2.64
UPK	0.0070	0 0070	1.00	1 30	2 24	0 0070	0.0056	0 80	1.15	1.98	0 0084	0.0070	0.83	1.20	2.07
CM	0.0070	0 0070	1.00	1.53	2.64	0.0070	0.0084	1.20	2 02	3.48	0.0056	0.0056	1 00	1.36	2.35
Original level (OL)	0.0063	0.0091	1.44	1.41	2.43										

		NH_3-N	NO_3-N	NO_3/NH_3	Organic carbon
C.D. at 5%	Fertilizer treatment	NS	0.0007*	NS	0.0675*
	Pesticide	NS	0.0005*	NS	NS
	Interaction	0.0028*	0.0012*	NS	0 1172*

* Significant

TABLE 1(b)—EFFICIENCY ORDER OF THE CHANGES SHOWN UNDER TABLE 1(a)

Factors	C_f	P_m	P_c
NH_3-N	Cont.>N=NPK=U=UPK=CM>OL	U>N=NPK=UPK=CM >OL>Cont.	U=UPK>Cont =NPK >OL>N=CM
NO_3-N	OL>Cont.=NPK=UPK=CM>N=U	OL>NPK=CM>N=U >Cont =UPK	OL>Cont =NPK=UPK>N =U=CM
NO_3/NH_3	OL>NPK=UPK=CM>Cont.>N=U	OL>Cont >NPK=CM>N >U>UPK	OL>Cont =N=NPK =CM>UPK>U
Organic carbon	CM>OL>NPK>U>UPK>N>Cont	CM>OL>U>UPK>NPK >N>Cont.	U>OL>CM>NPK>UPK >N>Cont.

TABLE 1(c)—GENERAL EFFICIENCY ORDER OF THE CHANGES SHOWN UNDER TABLE 1(a)

Factors	NH_3-N	NO_3-N	NO_3/NH_3	Organic carbon
Pesticide	$C_f>P_c>P_m>OL$	$OL>P_m>C_f>P_c$	$OL>P_m>P_c>C_f$	$OL>P_c>P_m>C_f$
Fertilizers	U>UPK>NPK>Cont =N=CM>OL	OL>NPK>CM>Cont =UPK>N=U	OL>NPK=CM>Cont. >N>UPK>U	CM>OL>U>NPK >UPK>N>Cont.
Interaction	$Cont_{(Cf)}=U_{(Pm)}=U_{(Pc)}$ $=UPK(P_c)$	$NPK_{(Pm)}=CM_{(Pm)}$ $>Cont_{(Cf)}=NPK_{(Cf)}$ $=UPK_{(Cf)}=CM_{(Cf)}=Cont_{(Pc)}$ $=NPK_{(Pc)}=UPK_{(Pc)}$	$Cont_{(Pm)}>NPK_{(Cf)}$ $=UPK_{(Cf)}=CM_{(Cf)}$ $=Cont_{(Pc)}=N_{(Pc)}$ $=NPK_{(Pc)}=CM_{(Pc)}$	$CM_{(Pm)}>CM_{(Cf)}>U_{(Pc)}$

OL = Natural soil ; C_f = Fertilizer treated soil
Pm = Fertilizer treated soil with metasystox
P_c = Fertilizer treated soil with carbofuran

carbofuran addition enhanced the formation of NH_3-N either by nitrogen fixation or by rapid decomposition of root residues to maintain a proper C/N ratio in the soil.

Since there was more nitrate absorption in presence of metasystox, the nitrogen content of the soil became less and to maintain a proper C/N ratio more carbon was lost from the soil to the atmosphere. Carbofuran applied soils thus recorded more organic carbon content than soils in which the plants were grown in presence of metasystox.

The status of different forms of nitrogen in the original soil and soils treated with fertilizers only, did not show a fixed tendency of nitrogen utilization/absorption although in general it appears that there was more ammonification and nitrification in the soils treated with the fertilizers. Under such a trend there would be more organic carbon content in comparison to the other treatments of pesticides which was not the case. In the original level of the soil, different forms of nitrogen and organic carbon, barring NH_3-N, NO_3-N, nitrification and

organic carbon were the highest in comparison to the other treatments.

Regarding interaction between fertilizers and the two pesticides it appears that the efficiency order of the soil in relation to the NH_3-N content treated with U and metasystox was the same as the control where no fertilizer was added. So was the case with the soil where U and UPK both were applied with carbofuran The maximum efficiency order in relation to the NO_3-N or nitrification was found in the soils treated with NPK and CM in combination with metasystox. Rate of nitrification was increased by the application of metasystox only than other treatments. However, as regards the interaction in relation to the organic carbon content of the soil it appeared that the soils treated with cowdung manure and metasystox is at the highest value followed by cowdung manure only and then urea treated with carbofuran.

It has been observed that for maximum NH_3-N content, interaction between fertilizer treatments and pesticides was significant statistically at 5% [Table 1(a)] For NO_3-N, fertilizer treatments, pesticides and their interaction with each other were statistically significant. For percentage of organic carbon, fertilizer treatment and its interaction with pesticides were also significant statistically.

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Retarding Influence of Phosphates and Wheat-straw on Nitrogen Loss in Soils Treated with Ammonium Sulphate and Ammonium Nitrate

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It has been observed that phosphates retard the nitrogen loss forming stable compounds like ammonium phosphate. Wheat-straw helped in checking the nitrogen loss and increasing the available N and P_2O_5 contents pH of the samples was also found to be affected by phosphate, nitrogen and carbon interactions This finding was substantiated by laboratory and pot experiments conducted with alluvial soils of Varanasi (U.P)

SUPPLY of readily available nitrogen is generally met by the application of nitrogenous fertilizers Inorganic nitrogen compounds like ammonium and nitrates usually suffer several types of losses from the soil viz., loss of nitrogen in the gaseous form, loss through immobilization, loss due to leaching etc. On account of such losses the recovery of nitrogen, when applied as fertilizer or manure, by crops is not high. Both the organic and inorganic fractions of the soil have the ability to react with the available forms of nitrogen in such a way as to make it unavailable to higher plants.

Sohn and Peach[1] have carefully studied the retention and fixation of ammonium applied as salts of strong acids to different soils. Allison *et al*[2] have shown that the presence of organic matter hinders the fixation of ammonia by blocking the entrance of ammonium ions between the clay plates Dhar[3] has also suggested the loss of nitrogen during ammonification and nitrification processes due to the formation of a very unstable substance, ammoniu nitrite, which decomposes very easily producing nitrogen gas.

An attempt has been made in this paper to investigate the influence of phosphates and wheat-straw on retardation of nitrogen loss in soils treated with ammonium sulphate and ammonium nitrate.

Experimental

200 g sandy loam soil from Varanasi (U P) passing through 50 mesh sieve was taken in dishes Required amounts of superphosphate, Trichinopoly rockphosphate, Tata basic slag and bone meal at the rate of 0.25% P_2O_5 and $(NH_4)_2SO_4$ and NH_4NO_3 at the rate of 0 1% N were incorporated in the dishes and thoroughly mixed with wheat-straw application at the rate of 0.5% carbon level.

Moisture was maintained at 20% level throughout the experimental period. At regular intervals of 60,120 and 180 days, composite soil samples were taken out from each set and were analysed for total carbon, available N, available P_2O_5 and *p*H. Methods of estimations employed are as mentioned by Jackson[4].

TABLE 1—ANALYSES OF SOIL AND FERTILIZER MATERIALS

	Estimation	Content	Estimation
Soil	*p*H	7.8	Wheat straw
	Total N	0.057%	Total C = 36 6%
	Total P_2O_5	0.138%	Total N = 0 616%
	Total CaO	0 894%	Superphosphate
	Total MgO	0 437%	Total P = 16.2%
	Total K_2O	0.994%	Rockphosphate
	Total C	0 601%	Total P = 23.6%
	Available N	40.0 ppm	Tata basic slag
	Available P_2O_5	4.6 ppm	Total P = 7.53%
	Sand	56 3%	Bone meal
	Silt	30.2%	Total P = 21.7%
	Clay	6.5%	Total N = 4 4%

Results and Discussion

The experimental results recorded in Tables 2 to 4 show that in all sets there is a marked loss of nitrogen after 60, 120 and 180 days. Nitrogen loss in ammonium sulphate sets has been observed to be higher as compared to ammonium nitrate ones. Phosphatic sources viz. rockphosphate, Tata basic slag and bone meal have been found to have significant influence over retention of nitrogen. Superphosphate being acidic in reaction does not seem to check the nitrogen loss. Application of phosphates along with 0.5% carbon introduction in the form of wheat-straw also help in checking the nitrogen loss. Available nitrogen content of the soil samples is also found to be influenced by the application of phosphates. Carbon introduction accelerated the availability of the nitrogen in all the sets which is revealed by data in Tables 2 to 4. *p*H values of the soil samples has also been found to be affected by the application of nitrogenous fertilizers, phosphates and wheat-straw. Effect of N and P fertilizers on soil *p*H variation has been reported by Volk and Tidmore[5], Grunes[6] and others.

TABLE 2—ANALYSES OF SOIL AFTER 60 DAYS WITH AMMONIUM SULPHATE AND AMMONIUM NITRATE AMENDMENTS

Treatment	Total C %	% N loss	Av. P_2O_5 ppm	Av. N ppm	pH
		With ammonium sulphate			
1. Control	0 057	32.0	4.6	51.0	7.6
2. S.P.	0 055	36.5	5.8	50.0	7.4
3. S.P.+W S.	0.061	30 0	5.9	50.5	7.3
4. R.P.	0 059	28 0	4.9	54.0	7 6
5. R.P.+W.S.	0 064	24 5	5.0	52.0	7 2
6. T.B S.	0 052	25.0	4.8	51 5	7.6
7. T.B.S.+W S	0 062	22 0	5.1	50.0	7.1
8. B.M.	0.055	20.5	5.0	55.0	7.5
9. B.M.+W.S	0 064	16.5	5.2	57.5	7.3
		With ammonium nitrate			
1. Control	0 059	28.0	4 8	53.5	7.8
2 S.P.	0 055	31.5	5 8	50.5	7.3
3 S P.+W S	0.063	26 0	6 0	54.5	7.3
4. R.P	0.060	25.0	4.9	58.5	7.6
5. R P+W.S.	0.068	20.0	5.8	65.0	7.2
6. T B.S	0 061	23.5	5.0	57.0	7.6
7. T.B S+W.S.	0.068	20.0	5.8	65.0	7.2
8. B.M.	0 060	21.0	6.0	56.0	7.4
9. B.M.+W.S.	0.066	18.5	6.7	63.5	7.2

S P superphosphate
W S. wheat-straw
R P rockphosphate
T.B S. Tata basic slag
B.M bone meal

TABLE 3—ANALYSES OF SOIL AFTER 120 DAYS WITH AMMONIUM SULPHATE AND AMMONIUM NITRATE AMENDMENTS

Treatment	Total C %	% N loss	Av P_2O_5 ppm	Av N ppm	pH
		With ammonium sulphate			
1. Control	0 054	40.0	5 0	47 0	7 6
2. S P.	0 051	47.0	6 2	45 5	7 4
3. S.P.+W S.	0 060	39.0	6.5	48 5	7 4
4. R P.	0.056	36.0	6.0	50.0	7.5
5 R P+W.S	0.062	31.5	6.7	51.5	7.4
6. T B S	0.055	34 5	6 2	55.5	7.5
7 T B S+W S.	0 060	26 0	6 7	57 0	7.5
8 B M.	0.050	28 5	6 3	53.0	7.3
9. B M.+W.S.	0.061	21 0	6.9	58.5	7.1
		With ammonium nitrate			
1 Control	0 054	35.5	5.3	49 5	7 8
2. S.P.	0.050	37 0	6.4	47.0	7.3
3 S P.+W S.	0.061	34 5	6.7	51.5	7.1
4. R.P.	0 054	30.0	6.5	55 0	7.5
5. R.P.+W.S.	0 059	27 5	6.9	57 5	7.4
6. T B.S.	0.056	27.0	6.4	53 0	7.4
7. T.B.S.+W.S.	0 061	25 0	6.9	61.5	7.2
8. B.M.	0.053	25 0	6 5	54.5	7.2
9. B.M+W.S	0 061	23 5	7 2	61.5	7.2

TABLE 4—ANALYSES OF SOIL AFTER 180 DAYS WITH AMMONIUM SULPHATE AND AMMONIUM NITRATE AMENDMENTS.

Treatment	Total C %	% N loss	Av. P_2O_5 ppm	Av. N ppm	pH
		With ammonium sulphate			
1. Control	0.049	46.0	5.2	48.2	7.6
2. S.P.	0.047	48.5	6.7	47.0	7.4
3. S P.+W.S.	0 057	40.0	7.3	50.0	7.3
4. R.P.	0.051	37.5	6.3	52.2	7.5
5. R.P.+W.S.	0.060	33.0	6.9	54.5	7.4
6. T.B.S.	0 052	37.0	6.3	56.0	7.5
7. T.B.S.+W.S.	0.060	29.0	6.9	59.0	7.5
8. B.M.	0.049	32.5	6 5	57.5	7.4
9. B.M.+W.S.	0.058	24.0	7.4	60.5	7.2
		With ammonium nitrate			
1. Control	0.050	40.0	5.0	44.0	7.5
2. S.P.	0.049	42.5	6.6	46.6	7.4
3. S.P+W.S	0.062	38.5	7.5	47.5	7.3
4. R.P.	0.051	35.0	6.4	58.0	7.5
5. R.P.+W.S.	0.057	30.0	6.9	62.5	7.4
6. T.B.S.	0.049	35.5	6.5	55.5	7.4
7. T B.S.+W.S	0.058	29.0	7.0	64 0	7.5
8. B.M.	0.049	30.0	6.6	57.0	7.4
9. B.M.+W.S.	0.057	23.5	7.6	67.0	7.3

TABLE 5—INFLUENCE OF PHOSPHATIC SOURCES AND WHEAT-STRAW ON N AND P UPTAKE BY WHEAT WITH AMMONIUM SULPHATE AND AMMONIUM NITRATE INCORPORATION

Treatment	Dry wt. g/pot	N uptake %	P uptake %	N/P ratio	Crude protein %
		With ammonium sulphate			
1 Control	10.8	1.08	0 365	2 95	6.75
2 S P	16.5	1.32	0.390	3.38	8 25
3 S.P+W.S.	18 0	1.48	0.425	3.48	9.25
4. R P	15 2	1 28	0 382	3 35	8 00
5. R P.+W.S.	16 5	1 41	0 392	3.59	8 80
6 T B S.	15.8	1 21	0.386	3 13	7.56
7. T B.S.+W.S.	17 8	1.29	0.392	3.29	8.06
8 B.M	15 5	1.30	0 388	3 35	8.12
9. B M+W S.	17.4	1 45	0 415	3.49	9.06
C.D. (5%)	1.69	0.26	0.041	0.29	1.64
		With ammonium nitrate			
1. Control	10.5	1 08	0.366	2 95	6.75
2. S.P.	16 0	1 30	0.386	3 36	8 12
3. S P+W.S.	16.8	1 45	0 420	3.45	9.06
4. R P	18 3	1.25	0.385	3.24	7 81
5. R P+W.S.	15.0	1 40	0.395	3.54	8 75
6. T.B S.	16.3	1.27	0 388	3 27	7.93
7 T.B.S+W.S.	18.0	1.32	0 395	3 34	8.25
8. B.M	15.5	1 30	0 390	3.33	8.12
9. B M.+W S.	17.9	1.40	0.410	3.41	8.75
C.D. (5%)	1.54	0 19	0.017	0.54	1.27

Role of phosphates in stabilising the available nitrogen and retarding the nitrogen loss in different sets may be due to production of ammonium phosphate which is more stable than nitrate and ammonical compounds. Carbon incorporation in the form of wheat-straw can also be significantly correlated with the increase in the available P_2O_5 and nitrogen contents of soil and also influence the C/N ratio and pH of the soil. pH may influence the solubility of the phosphates which help the release of more available P_2O_5 for the plants.

Increase in the availability of phosphates by adding carbonaceous matter may be due to the production of carbonic acid and other organic acids by decomposition of wheat-straw. Estimation of total carbon of the soil samples was also conducted in all the sets and it has been observed that the oxidation of carbon is higher in treatments where wheat-straw and phosphate have been incorporated.

A pot experiment has been conducted with the same soil sample by growing wheat variety RR_{21} as test crop. It is observed that uptake of nitrogen is higher in treatments receiving phosphates and wheat-straw which show similar trend of results as obtained in the laboratory experiment. Increased

available P_2O_5 content of soil caused by the addition of phosphates and organic material incorporation might have resulted in the higher dry matter production as recorded in Table 5. Caldwell[7] also found increased crop uptake from P^{32} labelled monocalcium phosphate when intimately mixed with ammonium sulphate, ammonium nitrate or ammonium chloride but not in separate application. The most likely chemical explanation of the beneficial effects of nitrogenous salts is an increase of the solubility of the phosphates or their reaction products.

Acknowledgement

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Role of Toxic Aromatic Compounds in Nitrogen Enrichment

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The formation of amino acids in systems not containing any source of nitrogen, utilising compounds having antiseptic properties such as phenol, resorcinol etc has been investigated and the results conclusively showed that nitrogen enrichment is a photochemical process and not purely a bacterial process. The energy required for this process is obtained by the oxidation of the carbonaceous compounds and by the photolytic fission of water.

GRÜITTONEON[1] observed nitrogen fixation by utilising toxic compounds such as phenols and salicylates. Dhar[2] and co-workers observed fixation of atmospheric nitrogen in the slow oxidation of various organic compounds such as glycerol, acetophenone etc by air, mixed with chemically pure surfaces such as Al_2O_3, TiO_2, Fe_2O_3 and ZnO etc. Hannequine[3] *et al* have reported the general occurence of *para*-hydroxybenzoic acid, vanillic acid and *para*-coumaric acids in certain soils. Dhar pointed out that the chemical energy liberated from the oxidation of carbohydrates, fats, etc, can enrich the system from nitrogen point of view, even in dark and in the absence of bacteria.

In the present work, we have carried out systematic investigations of nitrogen fixation using aromatic toxic organic compounds such as phenol, resorcinol which can destroy bacteria. Russel and Buddin[4] found that the antiseptic compounds such as phenols and cresols, when used in their experiments of nitrogen fixation destroyed the microorganisms Light plays an important role in many chemical reactions and hence the influence of light on carbon-nitrogen transformations has also been studied.

Experimental

200 g of sieved and oven dried titania were taken in 500 ml conical flasks. To this, required quantities of phenol or resorcinol and phosphates were introduced as 1% carbon and 0 5% P_2O_5 as $CaHPO_4$ $2H_2O$, respectively. The contents of each flask were thoroughly mixed and the mixture made uniform. Two identical sets were arranged side by side, one of which was exposed to sun light and the other was covered with a thick black cloth. In all the experimental flasks the moisture content was maintained at 40% level throughout the experiment. All these flasks were plugged with cotton wool.

For the sterile sets, the entire above process was repeated and then all flasks sterilised for 20—30 min at 15 lbs pressure and at 115°, before exposing to light.

After definite intervals of time the contents of one flask from each set (sterile, unsterile, exposed and covered) was well ground and transferred into a 250 ml volumetric flask and the volume made up with water. An aliquot was taken and evaporated on a waterbath with a drop of conc. H_2SO_4 to prevent the escape of ammonia, and analysed for total nitrogen and total carbon according to the methods of Robinson, Mclean and Williams[5] and of Treadwell and Hall[6], respectively. For other estimations the standard methods were used.

Discussion

From the experimental record it is interesting to note that nitrogen has been observed in the systems containing phenol and resorcinol which are well known germicidals and thus the possibilities of bacterial fixation of nitrogen can easily be ruled out. These results bring out the marked significance of surface and light in oxidation reactions as the oxidation of carbon in the sets exposed to light in both sterile and unsterile conditions is a combination of photochemical, surface and catalytic reactions while the oxidation of carbon in the covered sets under sterile conditions, where microbial and light actions are ruled out, is purely a surface and catalytic process. Thus it is clear from these results that surface and catalytic reactions accelerated by light absorption play an important role in the transformation and oxidation of organic compounds and fixation of atmospheric nitrogen. Dhar postulated that the important photochemical reaction involved in plant photosynthesis was the decomposition of water by the absorption of light. In explaining the process of nitrogen fixation, the best mechanism seems to be the same, i.e., decomposition of water into $\dot{H}$ and $\dot{O}H$ by the absorption of energy obtained from the oxidation of energy rich materials like glucose, cellulose, lignin, fat etc as follows :



$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 676 \text{ K cal.}$$



$$H_2O + 112 \text{ K cal.} = \dot{H} + \dot{O}H$$



$$\text{i.e. } 6H_2O + 672 \text{ K.cal} = 6\dot{H} + 6\dot{O}H$$

TABLE 1—200 g TITANIA + 40% MOISTURE (CONTROL). AVERAGE TEMPERATURE = 34°

UNSTERILE SETS

Period of exposure in days	Total Carbon (g)	Total Nitrogen (g)	Efficiency	NH_3-N (g)	NO_3-N (g)	Amino acids identified chromatographically	Amount of aminoacids with respect to glycine (g)	Available P_2O_5 (g)
					LIGHT			
0	0.0426	0 0082	—	–	0 0016	–	–	0 0086
60	0 0276	0.0085	20.0	0.0002	–	–	–	0.0091
120	0 0228	0.0086	20 4	0 0003	–	–	–	0 0098
240	0 0173	0.0087	19.4	0 0003	0.0017	Gly, Al, Glu, Va	0.0265	0 0101
					DARK			
0	0.0426	0 0082	–	–	0 0016	–	–	0 0086
60	0 0320	0.0083	10 2	–	–	–	–	0 0088
120	0.0250	0 0084	11.2	–	–	–	–	0.0090
240	0 0196	0.0085	9.8	0.0002	–	–	–	0 0092

TABLE 2—200 g OF TITANIA + 1% C AS PHENOL + 40% MOISTURE

					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.0086
60	1.6531	0.0213	33 8	0 0026	0.0050	Gly, Al, Va, Glu	0.4349	0.0098
120	1.3775	0 0309	34 2	0.0032	0.0062	Gly, Al, Va, Glu, Asp	0 7862	0.0104
240	1 0186	0.0414	32 5	0.0035	0.0067	Gly, Al, Va, Glu, Asp, Threo	0.9275	0.0110
					DARK			
0	2.0426	0.0082	–	–	0 0016	–	–	0 0086
60	1.7979	0.0119	15.2	0.0011	0.0020	Gly, Al	0 945	0.0095
120	1.6764	0.0154	15.6	0.0015	0.0028	Gly, Al, Glu, Asp	0 1273	0.0098
240	1.3111	0.0183	13.8	0.0017	0 0030	Glu, Gly, Al, Va, Asp, Threo	0 1489	0.0100

TABLE 3—200 g TITANIA + 1% C AS RESORCINOL + 40% MOISTURE

					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0 0086
60	1.6303	0.0234	37.0	0.0031	0.0060	Gly, Al, Va, Glu	0 7866	0 0112
120	1.3140	0.0355	37.6	0.0036	0 0069	Gly, Al, Va, Glu, Asp	1 5169	0.0118
240	0.9140	0.0492	36.4	0.0039	0.0076	Gly, Al, Va, Glu, Asp, Threo	1 5632	0.0125
					DARK			
0	2.0426	0 0082	–	–	0.0016	–	–	0.0086
60	1.7751	0.0130	18.0	0 0014	0 0028	Gly, Al	0 1037	0.0098
120	1.5597	0.0169	18.5	0.0019	0.0036	Gly, Al, Glu, Asp	0 1549	0.0102
240	1.2759	0.0208	16.5	0.0022	0.0040	Gly, Al, Glu, Asp, Va, Threo	0 1567	0.0105

TABLE 4—200 g TITANIA + 1% C AS PHENOL + 0.5% P_2O_5 AS $CaHPO_4.2H_2O$

					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	—	0.4572
60	1.4556	0.0377	50.4	0.0051	0.0084	Gly, Al, Va, Glu, Se	0 6836	0.4683
120	1.1618	0.0515	51 2	0.0058	0.0098	Gly, Al, Va, Glu, Se, Asp	0 9887	0.4786
240	0.7422	0.0721	49.2	0.0063	0.0104	Gly, Al, Va, Glu Se, Asp, Treo	1 2651	0 4804
					DARK			
0	2.0426	0.0082	–	–	0.0016	–	–	0 4572
60	1.6813	0.0176	26.2	0.0027	0 0048	Gly, Al	0 1850	0.4587
120	1.4751	0.0234	26.8	0.0035	0.0054	Gly, Al, Glu, Asp	0.2965	0.4639
240	1.0802	0.0322	25.0	0.0039	0.0059	Gly, Al, Glu, Asp, Threo, Se	0.3073	0.4679

TABLE 5—200 g TITANIA + 1% C AS RESORCINOL + 0.5% P_2O_5 AS $CaHPO_4.2H_2O$

					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1.4361	0.0407	53.6	0.0056	0 0093	Gly, Al, Va, Glu, Se	1.0236	0.4692
120	1.1421	0.0572	54.4	0.0063	0.0105	Gly, Al, Va, Glu, Se, Asp	1.9562	0.4814
240	0.7237	0.0767	82.0	0.0068	0.0110	Gly, Al, Va, Glu, Se, Asp, Threo	2 0313	0.4871
					DARK			
0	2.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1.6705	0.0184	27.4	0.0030	0.0052	Gly, Al	0.2006	0 4594
120	1.4615	0.0244	28.0	0.0037	0 0059	Gly, Al, Glu, Asp	0.3117	0.4648
240	1.0709	0.0344	27.0	0.0042	0.0064	Gly, Al, Glu, Asp, Va, Threo, Se	0.3200	0.4690

TABLE 6—200 g TITANIA +1% C AS PHENOL +40% MOISTURE STERILE SETS AVERAGE TEMPERATURE = 34°

Period of exposure in days	Total Carbon (g)	Total Nitrogen (g)	Efficiency	NH_4-N (g)	NO_3-N (g)	Amino acids identified chromatographically	Amount of aminoacids with respect to glycine (g)	Available P_2O_5 (g)
					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.0086
60	1.6777	0.0193	30 6	0.0019	0.0037	Gly, Al, Va, Glu	0.3456	0.0094
120	1.4213	0.0275	31.2	0.0025	0.0046	Gly, Al, Va, Glu, Asp	0.5374	0.0099
240	1.1338	0.0353	29.8	0.0028	0.0052	Gly, Al, Va, Glu, Asp, Threo	0.7361	0.0105
					DARK			
0	2.0426	0.0082	–	–	0.0016	–	–	0.0086
60	1.8241	0.0111	13.4	0.0007	0.0018	–	–	0.0090
120	1.6273	0.0139	13 8	0 0011	0.0022	–	–	0.0094
240	1.3792	0.0160	11 8	0.0013	0.0025	Gly, Al, Glu, Asp, Va	0.632	0.0297

TABLE 7—200 g TITANIA +1% C AS RESORCINOL +40% MOISTURE

Period of exposure in days	Total Carbon (g)	Total Nitrogen (g)	Efficiency	NH_4-N (g)	NO_3-N (g)	Amino acids identified chromatographically	Amount of aminoacids with respect to glycine (g)	Available P_2O_5 (g)
					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.0086
60	1.6573	0.0211	33.6	0.0023	0.0041	Gly, Al, Va, Glu	0.4693	0.0098
120	1.3928	0.3304	34.2	0.0029	0.0054	Gly, Al, Va, Glu, Asp	0.8732	0.0103
240	1.0952	0.0392	32.8	0.0033	0.0062	Gly, Al, Va, Glu, Asp, Threo	0.9621	0.0109
					DARK			
0	2.0426	0.0082	–	–	0.0016	–	–	0.0086
60	1.7995	0.0118	14.8	0.0011	0.0022	–	–	0.0092
120	1.5961	0.0150	15.4	0.0016	0.0030	–	–	0.0096
240	1.3354	0.0173	13.0	0.0019	0.0035	Gly, Al, Glu, Asp, Va	0.0893	0.0099

TABLE 8—200 g TITANIA +1% C AS PHENOL +0.5% $CaHPO_4.2H_2O$ +40% MOISTURE

Period of exposure in days	Total Carbon (g)	Total Nitrogen (g)	Efficiency	NH_4-N (g)	NO_3-N (g)	Amino acids identified chromatographically	Amount of aminoacids with respect to glycine (g)	Available P_2O_5 (g)
					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1.4961	0.0339	46.6	0.0032	0 0060	Gly, Al, Va, Glu, Se	0.5061	0.4603
120	1.2246	0.0468	47.2	0.0040	0.0072	Gly, Al, Va, Glu, Se, Asp	0.8376	0.4649
240	0.8241	0.0630	45.0	0.0045	0.0055	Gly, Al, Va, Glu, Se, Asp, Threo	0.9653	0.4690
					DARK			
0	0.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1.7144	0.0156	22.8	0.0020	0.0038	–	–	0.4579
120	1.5129	0.0196	23.4	0.0026	0.0050	Gly, Al, Glu	0.1004	0.4548
240	1.1251	0.0274	21.0	0.0030	0.0058	Gly, Al, Glu, Asp, Va, Threo	0.1732	0.4589

TABLE 9—200 g TITANIA +1% C AS RESORCINOL +0.5% P_2O_5 AS $CaHPO_4.2H_2O$ +40% MOISTURE

Period of exposure in days	Total Carbon (g)	Total Nitrogen (g)	Efficiency	NH_4-N (g)	NO_3-N (g)	Amino acids identified chromatographically	Amount of aminoacids with respect to glycine (g)	Available P_2O_5 (g)
					LIGHT			
0	2.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1.4774	0.0355	48.4	0.0037	0.0064	Gly, Al, Va, Glu, Se	0.7937	0.4634
120	1.1955	0.0497	49.0	0.0045	0 0076	Gly, Al, Va, Glu, Asp, Se	1.1463	0.4692
240	0.7845	0.0667	46.5	0.0050	0.0086	Gly, Al, Va, Glu, Asp, Threo	1.1704	0.4737
					DARK			
0	2.0426	0.0082	–	–	0.0016	–	–	0.4572
60	1 7047	0.0164	24.4	0.0023	0.0042	–	–	0.4583
120	1.4995	0.0217	25.0	0.0029	0.0050	Gly, Al, Glu	0.1337	0.4591
240	1.1001	0.0293	22 4	0.0035	0.0063	Gly, Al, Glu, Asp, Va, Threo	0.1982	0.4598

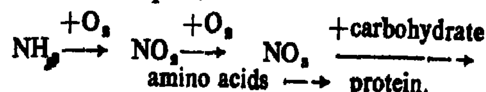
Gly = Glycine, Al = Alanine, Glu = Glutamic acid, Va = Valine, Asp = Aspartic acid, Threo = Threonine, Se = Serine

and this reaction is followed by the chemical combination of atomic hydrogen with atmospheric nitrogen leading to the formation of ammonia :



$$N_2+6\dot{H}=2NH_3$$

In the presence of sunlight, energy from the sun is absorbed by the system and is utilised in increasing the nitrogen fixation. The experiments of Bohr[7], Einstein[8] and Saha[9] have shown that nitrogen molecules become active and partially ionised due to the ultraviolet radiations of wavelength between 2900 Å to 3200 Å. This active nitrogen facilitates its reaction with atomic hydrogen forming ammonia. The ammonia formed readily undergoes oxidation and forms nitrite and nitrate which finally forms amino acids and protein.



$$NH_3 \xrightarrow{+O_2} NO_2 \xrightarrow{+O_2} NO_3 \xrightarrow{+\text{carbohydrate}} \text{amino acids} \longrightarrow \text{protein.}$$

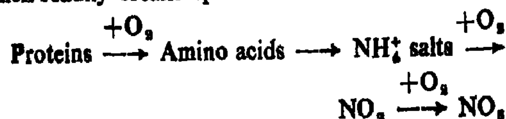
There is no doubt that both essential and non-essential amino acids are created in the system in the process of atmospheric nitrogen fixation caused by the energy liberated in the slow oxidation of organic compounds like phenol and resorcinol. It seems that the amino acids obtained with phenol

and resorcinol are almost the same and they appear to be derived from the process of fixation of atmospheric nitrogen on titania surface.

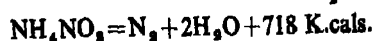
The phosphated and exposed sets are richer in amino acids than the unphosphated and covered sets. No amino acid could be detected in the covered sets under sterile condition during the first 120 days. In the covered and phosphated sets under sterile condition a few amino acids could be detected after 60 days.

These observations clearly show the marked influence of light on nitrogen fixation and subsequent utilisation of the fixed nitrogen in the formation of amino acids. It is also clear from these observations that when dicalcium phosphate was added to the system, not only did the efficiency of nitrogen fixation increase but the rate of fall of efficiency of nitrogen fixation was checked and the amount of nitrogen fixed both under sterile and unsterile conditions also increased.

During the process of ammonification and subsequent nitrification of amino acids and proteins, the highly explosive and unstable substance ammonium nitrite is formed as an intermediate which readily breaks up



$$\text{Proteins} \xrightarrow{+O_2} \text{Amino acids} \longrightarrow NH_4^+ \text{ salts} \xrightarrow{+O_2} NO_2 \xrightarrow{+O_2} NO_3$$



$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K.cals.}$$

liberating energy, nitrogen gas and water, which causes the fall in efficiency with the lapse of time.

But in the presence of dicalcium phosphate containing Ca^{2+} ions, the more stable compound, calcium nitrite is produced instead of ammonium nitrite. Moreover, in the presence of phosphates more or less stable phosphoproteins are formed and they seem to resist the ammonification and nitrification processes and check nitrogen loss and thus increase the nitrogen status of the system.

When the energy materials undergo slow oxidation some organic acids may be produced in the system. It is well known that the decomposition of ammonium nitrite (NH_4NO_2) is accelerated in presence of acids. But in presence of dicalcium phosphate which acts as a buffer the increase of the H^+ ion concentration of the system is not appreciable. Hence the efficiency of nitrogen fixation is greater in presence of dicalcium phosphate than in its absence.

It appears therefore that for nitrogen fixation neither soil nor bacteria are absolutely essential; what really seems indispensable is a suitable solid surface where water, oxygen, nitrogen and an energy material are properly absorbed and are in intimate contact, so that the slow oxidation of the energy material leading to liberation of energy and subsequent nitrogen fixation can be possible.

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Functional Approach to the Problem of Origin of Life—Photochemical Splitting of Water and Reduction of Nitrogen and Carbon dioxide

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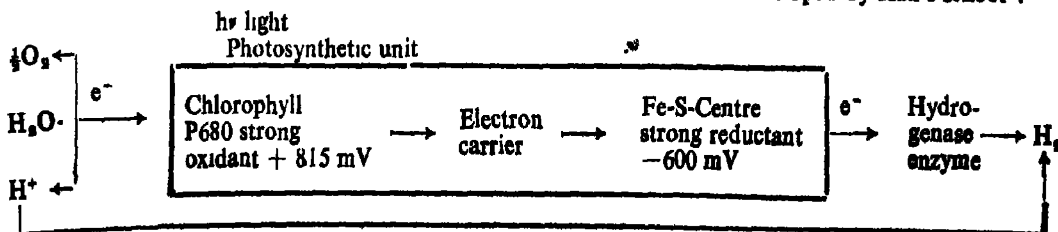
Jeewanu, the protocells, synthesised by the action of light on sterilised aqueous mixtures of simple organic and inorganic substances have many of the properties of biological order Ammonium molybdate *Jeewanu* and thiocyanate *Jeewanu* are characteristicin their ability of splitting of water molecule in sunlight and of fixation of inorganic carbon and nitrogen Unlike the many minerals which are extensively used at present for photochemical splitting of water, *Jeewanu* needs a night dark phase for reviving its ability to split water molecule and to reduce inorganic carbon. Both these processes need *Jeewanu* structure whereas nitrogen fixation can be affected even with materials left over after the breakdown of *Jeewanu* The photobiological like splitting of water by *Jeewanu* may be exploited for utilising solar energy for fixation of inorganic carbon and molecular nitrogen.

THE most important work utilising sunlight as the means of increasing the soil nitrogen is the investigations of Professor N. R. Dhar[1] and is being carried out for the last four decades. For the production of artificial nitrogenous manure a cheap source of hydrogen is needed and this is hydrogen from water, but water needs about 68 K cal per mole energy for its breaking up into hydrogen and oxygen.

To find a way out of the energy crisis, an understanding of the processes that took place during the period when life forms were originating is necessary. Abelson's view[2] is that the secondary atmosphere in which life originated consisted of N_2, CO_2 and H_2O Sillen[3] and Rutten[4], as a result of equilibrium calculations, came to the conclusion that "equilibrium conditions seem to exclude the formation of the 'thin soup' in the normal oceanic conditions even under an anoxygenic atmosphere". Perhaps there was an acute shortage of organic carbon in the hydrosphere when life came into existence The only possible way life could originate on the earth was that the earliest living systems had the ability to split water to hydrogen and oxygen deriving the energy from sunlight and to utilise the proton thus set free for the reduction of N_2 or CO_2 to ammoniacal nitrogen and organic material

The plants utilise radiations between 400 and 700 nm, which is photosynthetically active radiation (PAR) This PAR is 50% of the total sunlight and on earth's surface has an intensity of 800–100 W/m^2. The energy needed to break water to hydrogen and oxygen is 68.3 K cal per gm mole, and this must be absorbed by the water to produce every mole of hydrogen. Since water is transparent to visible solar radiation from 350 to 750 nm and does not absorb light greater than $\lambda>200$ nm, direct decomposition of water by solar radiation is not possible and the process needs sensitizers and/or catalysts. Many redox-dyes and pigments have been reported in the liberation which act as sensitizers in photooxidation and photoreduction of water. In plants, photosynthesis is carried out by the chloroplasts where photolysis of water is carried out by the concerted action of chlorophyll which absorbs the protons and the Mn-enzyme of photosystem II which acts as charge storage catalyst. The synthesis of ATP and $NADPH_2$ occurs and these are the two components needed for the reduction of CO_2 to carbohydrate.

In vitro system containing chloroplast-ferredoxin-hydrogenase, on illumination causes the liberation of oxygen and hydrogen The protons liberated at photosystem II are converted to hydrogen molecules by the hydrogenase. Benemann *et al* in 1973 suggested the possibility of using this system for commercial production of hydrogen[5]. The idea was later developed by Hall's school[6].



Solar energy has been converted to chemical energy using heterogeneous photocatalytic reactions and thus chemical compounds synthesised[7,8].

Photogenerated carriers, electrons and holes, in the space charge layer of a semiconductor electrode can be transferred to the reactants in an electrolyte solution and cause the photo-assisted decomposition or synthesis of chemical compounds[9,10]. Semiconductor catalysts may be assumed to undergo charge transfer across a solid-liquid junction similar to that in semiconductor electrodes, i e., charge transfer between semiconductor and redox reagents in solution would take the form of a conductance band and a valence band.

Functional properties of Jeewanu : With the above background of the work on photochemical splitting of water and reduction of N_2 and CO_2 by inorganic catalysts, the *Jeewanu* particles were examined because these have several properties of biological order and in all probability particles like these were immediate precursors of cellular life. In photobiological splitting of water into hydrogen and oxygen ferredoxin plays an important role of electron transfer and it is observed in several algae.

The work on *Jeewanu* was published in 1963[11,12] and independently confirmed by Briggs in 1964[13] and again in 1965[14]. In 1980 it was reported that *Jeewanu* have ability of splitting water molecule in sunlight and also of photochemical fixation of nitrogen and carbon dioxide by the photolysis of water[15].

Jeewanu, produced by the action of sunlight on sterilised aqueous mixture containing ammonium molybdate, diammonium hydrogen phosphate, biological minerals and formaldehyde have properties of growth, multiplication and metabolic activity[11,12]. Elemental analysis of *Jeewanu* indicated that it contains C, 13.87 ; H, 2 87 ; N, 9 22 ; Mo, 39.21 and P, 2 21%[16]. *Jeewanu* contain other elements as Fe, 0.18 , Mn, 0 005 ; Mg and K 0 003 ; Ca, 0 006 and Na, 0.10%[17]. These particles have a boundary wall and internal structures[18,19]. They can be fixed with biological fixatives, stained with biological dyes[28] and have many of the biochemicals of the cells such as amino acids in free form and peptide combinations, nucleic acid bases and nucleosides[20,21], phospholipids[22], a number of sugars such as glucose, fructose, ribose, deoxyribose[23] and a number of organic acids. These particles have material with esterase, catalase[13,14], phosphatase, ATPase, urease and peroxidase like activities[16] and are sensitive to the presence of antibiotics in the environment[24,25].

As ferredoxin has been found in all the cells, *Jeewanu* were tested for the presence of ferredoxin-like material in them with positive results[26-28].

The two constituents of nitrogenase are one, a Fe-S-protein and the other, a Mo-Fe-S-protein. If Fe-S-protein function could be performed by the ferredoxin-like material of *Jeewanu* and a large concentration of molybdenum could form a material similar in action to Mo-Fe-S-protein part of nitrogenase, perhaps *Jeewanu* could fix molecula[r] nitrogen and show the properties of nitrogenase like material. With this understanding a search fo[r] nitrogenase-like activity in *Jeewanu* was undertaken It was found that *Jeewanu* and water mixture, o[n] irradiation with light from Xenon lamp, showe[d] the conversion of acetylene in the overhead spac[e] of the irradiated mixture to ethylene. It wa[s] further observed that if D_2O is used instead o[f] H_2O, the ethylene formed is CHD=CHD indicatin[g] that it is the proton from H_2O which reduced CH≡CH to CH_2=CH_2[29].

It was observed that if purified CO_2 is bubble[d] through a mixture of *Jeewanu* and water while it i[s] exposed to sunlight a part of CO_2 is converte[d] to unsaturated hydrocarbon[30] and some of it i[s] converted to organic material soluble in th[e] irradiated mixture A night phase is neede[d] for the reactivation of the particles next da[y] (Table 1). Similarly, it was observed that i[f] bicarbonate is used as the source of inorganic carbo[n] *Jeewanu* are able to convert it to organic materia[l] on exposure to sunlight in aqueous mixture Optimum fixation is obtained when the conc. o[f] $NaHCO_3$ per ml of distilled water is 5 mg an[d] *Jeewanu* 1 mg and the air, freed of CO_2 an[d] O_2 by passing through pyrogallol and caustic sod[a] solution, is gradually passed through the irradiate[d] mixtures. Fixation of nitrogen is also observed an[d] a part of the nitrogen of the overhead is converte[d] to fixed nitrogen. This nitrogen fixation is no[t] affected by varying the concentrations of bicarbonat[e] in the irradiation mixtures There is a sligh[t] decrease in nitrogen fixation in all the flasks havin[g] $NaHCO_3$ but this decrease is the same at all th[e] concentrations of $NaHCO_3$ (Table 2).

TABLE 1– MILLILITRES OF 0.001 *N* $KMnO_4$ SOLUTION NEEDED FOR THE NEUTRALISATION OF UNSATURATED HYDROCARBONS FORMED IN 50 ml DISTILLED WATER, TRAPPING EVOLVED GASES FROM THE IRRADIATED MIXTURE OF *Jeewanu*, ON PASSING CO_2 THROUGH IT

Exposure days	Exposure time (in hours) 0	1	2	3	4	5	6
1	2 05	5.00	6.70	7.00	6.10	5.50	5.00
2	2 05	5.40	5 85	7.15	6.75	5.95	5.00
3	2 05	6.10	7.05	6.66	6.30	6.35	5.00
4	2 05	5.70	7.00	6.35	5.90	4.85	4.75
5	2 05	5.50	6 05	5.50	5.15	4.45	4.00
6	2.05	4.20	4.75	4.00	3.40	3.40	3.10
7	2.05	4.00	4 25	4.00	3.40	3.15	3.00
8	2.05	3.80	3.85	3.50	3.20	2.65	2.55
9	2.05	3.25	3.35	3.00	3.00	2.45	2.10
10	2 05	2.85	3 00	2.70	2.50	2.20	2.05
11	2.05	2.45	2.65	2.30	2.15	2.05	2.05
12	2.05	2.10	2.15	2.05	2.05	2.05	2.05

AMOUNT OF ORGANIC CARBON (mg) FORMED PER 2.0 ml OF IRRADIATED MIXTURE HAVING *Jeewanu* ON PASSING CO_2 THROUGH IT, FOR 6 hr OF EXPOSURE TO SUNLIGHT IN A DAY

	Exposure time (days) 0	2	4	6	8	10	12
Amount of organic carbon (mg)	0.205	0.306	0.383	0.434	0.485	0.510	0.53

TABLE 2—ORGANIC CARBON (mg) FORMED PHOTOCHEMICALLY BY 2.0 ml OF *Jeewanu* MIXTURES HAVING DIFFERENT CONCENTRATIONS OF $NaHCO_3$

Amount of $NaHCO_3$ per 100 ml of the mixture (mg)	Exposure time (hours)							
	0	6	12	18	24	30	36	42
Control	0.178	0.180	0.180	0.183	0.183	0.183	0.185	0.185
50	0.178	0.196	0.215	0.228	0.236	0.244	0 251	0.256
100	0.180	0.205	0.229	0.246	0 257	0 267	0 276	0.281
500	0.183	0.236	0.308	0.357	0 397	0 434	0 464	0 482
750	0.185	0.231	0.295	0.333	0.366	0.401	0.431	0.451
1000	0.187	0.215	0.241	0.262	0 281	0.294	0.305	0 317

AMINO NITROGEN (mg) FORMED PHOTOCHEMICALLY BY 2.0 ml OF *Jeewanu* MIXTURES HAVING DIFFERENT CONCENTRATIONS OF $NaHCO_3$

Amount of $NaHCO_3$ per 100 ml of the mixture (mg)	Exposure time (hours)							
	0	6	12	18	24	30	36	42
Control	0.171	0 222	0 257	0.299	0.339	0.367	0.390	0.415
50	0 171	0.219	0.253	0.293	0.322	0.347	0.374	0 402
100	0.171	0.217	0.253	0.290	0.321	0 344	0 371	0.399
500	0.172	0 217	0.251	0.285	0.312	0 366	0.360	0.381
750	0.172	0.217	0.250	0.281	0.306	0.324	0.343	0.362
1000	0 172	0.217	0 250	0.274	0.296	0.318	0.341	0.361

The above results show that fixation of CO_2 and nitrogen are effected by two different sets of enzymes after hydrogen is made available by the splitting of water. Further investigations revealed that in the fixation of CO_2 the structure of *Jeewanu* is important and once the structure is destroyed completely the fixation of CO_2 stops. For the fixation of nitrogen no structure is needed and it can proceed even when the structure of *Jeewanu* is completely destroyed leaving only the chemical constituents in the irradiation mixture.

The work on fixation of HCO_3^- carbon was repeated using $H^{14}CO_3^-$ and it was observed that ^{14}C is present in the organic material formed in the irradiated mixture[29].

Investigation of the photolytic splitting of water by *Jeewanu* alone was undertaken. It was observed that if a mixture of *Jeewanu* and water is thoroughly shaken and exposed to sunlight, bubbles of gas start coming out of the mixture after about 10 to 15 min. The liberation of gas continues for about 1 hr. The bubbles of gas come out from the bottom of the tube where the particles settle down. If sunlight is cut off the liberation of gas bubbles stops.

Our first reaction was that the liberated gas may be the dissolved air in the mixture which came out of the mixture when it became warm due to the heat of the sunlight if these *Jeewanu* have an extraordinary property of absorbing a lot of air. So after the mixture stopped giving out gas bubbles after about 1 hr of sunlight exposure, it was cooled to room temperature, thoroughly shaken to provide the condition for optimum absorption of air by the particles and exposed. Another crop of gas bubbles was obtained. However, when the liberation of gas stopped again after the next hour, the process of cooling, shaking and exposure was repeated. It was found that only a few gas bubbles come out the third time and that too for a short while. On repeating this process several times the same day, it was observed that the particles stopped giving out gas bubbles though optimum condition for the absorption of air by the particles was provided each time. This indicates that the gas bubbles which come out of the particles on exposure to sunlight are not of the dissolved or adsorbed air. Moreover, a control mixture which did not have *Jeewanu* but other inorganic solids did not show any liberation of gas. This showed that *Jeewanu* have the property of splitting water.

The *Jeewanu*, after about a few times of cooling, shaking and exposure, were in capable of gas liberation on that particular day. When these *Jeewanu* rendered inactive after a few times of cooling, shaking and exposure to sunlight on a single day, are allowed to stand overnight in the dark, they become active again for the liberation of gas (Table 3).

In another experiment two similar mixtures were prepared and their ability to liberate gas was exhausted by repeated cooling, shaking and exposure to sunlight. One mixture was then kept in the dark through the night and the other one was allowed to stand 1 meter away from a 1000 watts tungsten filament lamp through the whole night It was observed the next morning that the mixture kept in the dark during the night had recovered and showed liberation of gas on exposure to sunlight but the mixture kept in light during the night had not. This indicated that a dark phase is essential for the reactivation of the *Jeewanu*.

It was further observed that if the *Jeewanu* are not shaken at all and are kept for exposure in sunlight after the night phase there is very little evolution of gas bubbles and during shaking after night some gas comes out of the mixture. It therefore appears that some transformation takes place in *Jeewanu* in the night and some gas is liberated but due to the contact of this gas with the particle an equilibrium sets in. This gas is driven out during shaking and creates conditions favourable for the splitting of water by *Jeewanu* in sunlight. Shaking during the day may also be doing the same in addition to bringing newer surface of *Jeewanu* in contact with light and splitting of water molecules takes place. It stops after some time when the surface of the particle in contact with light is rendered useless for the reaction. This surface is reactivated next day after the dark phase.

Manometric experiments using Warburg's flask: The experiments were then performed with Warburg's flasks.[a] Three similar Warburg's flasks of total volume 14.5 ml each were taken and their manometers were filled with mercury. The first flask had 5 ml distilled water in the main vessel and 0.3 ml distilled water in the side arm; this acted as the control. The second flask had 5 ml distilled water and 10 mg *Jeewanu* in the main vessel and

TABLE 3 – LIBERATION OF GAS BUBBLES PER MINUTE ON EXPOSURE OF THE MIXTURE TO SUNLIGHT BY HIGH MINERAL *Jeewanu*

Number of gas bubbles (Arithmetic mean and statistical average)

	Exposure time (minutes)					
	10	20	30	40	50	60
1st day	14 8±1 98	27.6±2.37	17 6±1.16	15 0±1 14	15.2±0.86	15.4±1.43
After 1st cooling and shaking						
	3.0±0.31	30 8±1.35	24.4±1.69	18 8±0.55	12.6±0.56	10.6±0.50
After 2nd cooling and shaking						
	14 8±1 01	20,0±0.74	17.2±0.73	11.4±1 02	8.6±1.28	6.6±0.50
After 3rd cooling and shaking						
	0.6±0.39	9.6±0.81	3.4±0 24	7 2±0 37	7.2±0.37	1.6±0.4
After 4th cooling and shaking						
	0.0±0.0	0.2±0.2	0.4±0.24	0 2±0.2	0.2±0.2	0.0±0.0
2nd day	16.4±0.68	26.2±0 58	26.4±2.42	18 0±1 04	17.2±1.04	16.0±1.71
After 1st cooling and shaking						
	39.8±2 11	56.0±0.70	38 2±1 28	33 6±0.50	28.2±1.0	22 0±0.70
After 2nd cooling and shaking						
	1.4±0.20	4.4±0.81	4.2±0.69	2.2±0 2	0.6±0.39	0.2±0.2
After 3rd cooling and shaking						
	20.0±0.70	38.4±1 31	34 8±0.80	30.6±0.60	19 2±1 2	16.0±0.7
After 4th cooling and shaking						
	0.0±0.0	0.2±0.2	0.2±0 2	0 0±0.0	0.0±0.0	0.0±0.0
3rd day	14.4±0.67	36.0±1.07	24.2±1.15	26.0±1.88	16.6±0.50	15.2±1.15
After 1st cooling and shaking						
	61.4±2.56	55.6±1.29	40.6±2.10	30.4±1.35	28.4±1.50	18.6±3.16
After 2nd cooling and shaking						
	3.0±0.31	17.2±1.83	11.6±0 67	11 4±0 50	8.8±0.37	17.8±0.96
After 3rd cooling and shaking						
	0.4±0.24	4.4±0.60	2 6±0.67	1.6±0 67	0.6±0 39	0 2±0.2
After 4th cooling and shaking						
	0.0±0.0	0.4±0.24	0.2±0.2	0 0±0 0	0.0±0.0	0.0±0.0
4th day	18 6±0.93	34 8±1.52	32 0±1 30	20.2±0.80	16 6±1 12	9 0±0.83
After 1st cooling and shaking						
	50 4±1.43	57 2±1.15	21.0±1 41	16 0±0 83	9 2±0.96	5 0±0.37
After 2nd cooling and shaking						
	8.0±0 44	12 8±0.73	10 0±1.22	6 4±0 67	4 8±0 33	3 6±0.43
After 3rd cooling and shaking						
	15 8±0 86	34.8±1 24	30 8±2 04	21 2±1 11	10 2±0 96	4 6±0 50
After 4th cooling and shaking						
	0 0±0.0	1 2±0 37	4 8±0 58	2 4±0.50	1 4±0 24	0 6±0.39

LIBERATION OF GAS BUBBLES PER MINUTE ON EXPOSURE OF THE MIXTURE TO SUNLIGHT AFTER EXPOSURE FOR 4 DAYS, AFTER 5 TIMES OF COOLING AND SHAKING EACH DAY. ONE MIXTURE WAS KEPT UNDER 1000 WATTS LAMP DURING NIGHT WHEREAS A SIMILAR MIXTURE WAS KEPT IN DARK DURING NIGHT

Number of gas bubbles (Arithmetic mean and statistical average)

	Exposure time (minutes)					
5th days	10	20	30	40	50	60
D	26 0±0 70	42 2±1 39	23 4±0 50	17 8±1 01	10 8±0 58	5 4±0.50
L	0.8±0.37	1 8±0.37	2 8±0 37	3 0±0 44	1 6±0 40	0 8±0.37
After 1st cooling and shaking						
D	12 6±0 93	35.0±1.34	19 8±1 65	17.4±1 02	11.4±1 36	9.6±0 68
L	12.0±1 41	26 6±1.12	19 2±1 35	7 6±0 86	5.2±1.15	4.4±0.81
After 2nd cooling and shaking						
D	15 0±0.70	16 8±0.58	8.6±0.52	5 8±0 48	6.2±0.58	4.4±0.24
L	13 6±0.68	13.0±0.50	6 2±0.73	3 0±0 44	1 2±0 20	1.4±0.24
After 3rd cooling and shaking						
D	0.0±0 0	2 2±0.58	3 6±0 40	3 0±0 31	1 8±0.37	0 6±0 39
L	0.0±0 0	0.4±0 24	0 0±0.0	0 2±0 2	0.0±0.0	0.0±0.0
6th day						
D	20.8±1.24	22 4±1.28	17 2±0 86	7 8±0.88	6 6±0.24	6.8±0 86
L	4.0±0 54	3 6±0.97	5.0±0 83	3.8±0.58	2.6±0.58	1 2±0.58
After 1st cooling and shaking						
D	21.8±1.59	18.2±1 06	10 6±0 50	8.0±0.59	8 4±0.50	5 6±0.50
L	7.6±0.92	5.0±1 09	2 4±0.24	0.4±0.24	0.4±0.24	0.2±0.24
After 2nd cooling and shaking						
D	10.4±0.81	6 0±0.54	3.4±0 24	2 6±0.24	1.6±0.28	0.6±0.39
L	5.2±0.58	4.4±0.68	0.4±0.24	0.2±0.20	0.0±0.00	0.0±0.0
After 3rd cooling and shaking						
D	0.2±0.2	4.2±0 48	3 2±0 24	2 6±0 24	1.4±0 24	0 8±0.2
L	0.0±0.0	0.4±0.24	0.0±0 0	0 0±0.0	0 0±0.0	0 0±0 0

D = mixture stored in dark during night
L = mixture stored in light during night.

0.3 ml distilled water in the side arm. The third flask had 5 ml distilled water and 10 mg *Jeewanu* in the main vessel and 0.3 ml alkaline pyrogallol solution in the side arm. This was to absorb oxygen of the flask. This third flask was allowed to stand in the room to allow the oxygen of the flask to be absorbed by pyrogallol. When sufficient absorption of oxygen took place, the tap of the manometer was opened to allow that volume of air to come in. After several such treatments, all the oxygen of the flask was completely absorbed and the manometer showed no difference in pressure. All the three Warburg's flasks with attached manometer were then fixed in a stand keeping them as close to each other as possible so that the temperature of all the three was the same during the experiment, and the whole unit was exposed to light. The side lobes of all the flasks were covered with black cloth to avoid photochemical decomposition of the alkaline pyrogallol and also to provide similar conditions in all the three sets. The manometer reading of the control was subtracted from the readings of the other two to account for changes due to fluctuations in temperature.

It was observed that on exposure to sunlight there was increase in pressure of both the flasks containing *Jeewanu* and water and the increase was more in the flask which had pyrogallol in the side arm. After about 1 hr the pressure increase stopped. The whole unit was then transferred to shade. There was rapid decrease in pressure in both the *Jeewanu* containing flasks and the decrease was more in the flask with alkaline pyrogallol in the side arm. This decrease in pressure also became slow and stopped after about 1 hr. When the whole unit was again exposed to sunlight the pressure increase in *Jeewanu* containing flasks was observed and when again put in shade, after one hour, a decrease in pressure was recorded. This processes could be repeated a few times each day and by the end there was considerable decrease in the pressure when the unit was exposed to light. Next day after the dark phase of the night the reaction started afresh.

In light, the water molecules break-up into hydrogen and oxygen. The hydrogen set free combines with the nitrogen of the overhead space of the flask and the oxygen is absorbed in the alkaline pyrogallol in the side arm. The water splitting reaction is light dependent whereas the combination of N_2 and H_2 is not. Both the reactions, however, are hindered by the presence of oxygen in the overhead space. When *Jeewanu* and water mixture is exposed to light both the reactions start. When the flasks are brought in shade, the splitting of water stops but the combination of nitrogen of the overhead space with hydrogen produced during exposure continues so long as hydrogen is present in the flask. This accounts for the decrease in the pressure of the flask in shade. After all the free hydrogen of the flask is consumed the reaction of N_2 and H_2 also stops and decrease in the pressure in shade also stops.

Of the several types of *Jeewanu* which have been prepared and their water splitting property in sunlight investigated, two types are important: one, which is formed by the action of light on sterilised aqueous mixture of ammonium molybdate, diammonium hydrogen phosphate, biological minerals and formaldehyde and are known as ammonium molybdate *Jeewanu*[16] and the other, which is produced by the interaction of ammonium thiocyanate, calcium acetate, potassium hydrogen phosphate, biological minerals and formaldehyde and are called thiocyanate *Jeewanu*[22]. The effect of different metallic ions as Mo, Mn, Co, Cu and Zn in the parental medium of thiocyanate *Jeewanu* on the water splitting ability of the *Jeewanu* has been investigated. Co has been found to appreciably accelerate the water splitting ability.

The ammonium molybdate *Jeewanu* have greater ability of splitting water in sunlight. It has been observed that if acetic acid is also used as a source of organic carbon in ammonium molybdate *Jeewanu* parental medium together with formaldehyde, *Jeewanu* produced in it have greater water splitting ability. This ability can also be accelerated by incorporating more minerals in the *Jeewanu* by increasing the mineral solution in the parental medium. If a large volume of biological minerals are added in the parental medium to begin with, the formation of *Jeewanu* is considerably hindered or can even be stopped with large excess of mineral solution in the parental medium of *Jeewanu*[16]. However, if the parental medium of *Jeewanu* is initially started with the usual necessary amount of biological minerals and after 1 hr of exposure, when some *Jeewanu* are already formed in the mixture, additional mineral solution is added, the particles formed on further exposure are a little less than the control in dry weight but have greater ability of splitting water.

On studying the effect of period of exposure of the parental mixture of *Jeewanu* to sunlight on the water splitting of *Jeewanu* it has been observed that this increases with increasing period of exposure of the parental mixture to a certain limit. Further exposure destroys this ability. The effect of storing *Jeewanu* in their parental environmental medium in wet condition, and in dry condition in contact with air or under dry anaerobic conditions has been studied and it has been observed that *Jeewanu* are best preserved in their parental environmental medium and then comes preservation of *Jeewanu* in dry condition under anaerobic condition. Freshly prepared *Jeewanu* are more active in splitting water and this ability starts decreasing after 8 to 10 days and remains only in traces after 18 days.

Studying the effect of *p*H it has been observed that best gas evolution is observed in phosphate buffer at *p*H 8. The effect of *p*H on the fixation of inorganic carbon and molecular nitrogen by *Jeewanu* has also been studied.

Jeewanu *as precursors of cellular life*: The most interesting part is that *Jeewanu* have properties of biological order. They grow from within, multiply by budding and have metabolic activity. They can adapt and thus evolve in mildly changing

environment. Confirming the work on *Jeewanu*, Dr. M. H. Briggs wrote[14] :

> "While the definition of 'life' and 'living' is a difficult problem, it can be said that these microscopic objects (*Jeewanu*) satisfy many of the criteria of living cells. It seems entirely probable that objects similar to those observed in the present experiments were formed in the oceans of the primitive Earth and were the immediate precursor of cellular life".

Jeewanu are quite different from coacervates of Oparin[31], microspheres of Fox[32] and marigranules of Egami[33] which are photochemically inert. It appears that the secondary atmosphere of the earth in which life originated consisted of N_2, CO_2, and H_2O^8 and not of CH_4, NH_3, H_2, and H_2O as earlier believed[34]. In the absence of hydrogen the atmosphere of CO_2, N_2, and H_2 was energy poor. There are also evidences to suggest that there was very little organic matter in the hydrosphere of the earth when life originated, what to say of the possibility of the 'primordial soup' of Haldane. Even at that time a number of inorganic catalysts and semiconductor surfaces were effecting water splitting utilising the energy of sunlight. The properties of these minerals were greatly modified and they became more effective in photochemical splitting of water when they came in contact with the organic material synthesised.

Nature's self-organising process was in operation[35,36] and cybernetics and feed back mechanism produced such structures which could have some of the properties of biological order. These could get stabilised and developed because of their ability of splitting water molecules into hydrogen and oxygen and effecting nitrogen and carbon dioxide fixation. This started a flow of energy through them providing still greater stability[37] and enabled these particles to develop and evolve.

Thus, it was not only in the beginning of life that water was selected for splitting, utilising sunlight and producing hydrogen for reduction of inorganic carbon to organic carbon and nitrogen to ammoniacal nitrogen so much needed for the sustenance of life and living forms but even today this ability of splitting water with sunlight is continuing and is providing all the energy needed by the living forms through photosynthesis, where hydrogen is used up for the reduction of inorganic carbon and O_2 is set free in the atmosphere.

The study of the process of life synthesis will not only provide information of how life came into existence], but if studied with functional point of view may also point the way out of the present energy crisis, by emulating the process of utilising solar energy for its conversion to chemical bonds as nature did a few billion years back to initiate the existence of living forms on the earth.

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Complex Polymetaphosphates of Strongly Electropositive Elements

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SYNTHESIS and characterisation of high molecular weight chain phosphates, e.g., Graham's salt $(NaPO_3)_n$ and related derivatives, have received considerable attention in recent years with the growing interest in the field of inorganic polymers and polyelectrolytes. Various aspects of their chemistry have been extensively reviewed[1-9]. Since the observations of Hall[10] in 1934, Graham's salt (called calgon, i.e., calcium gone) has been extensively employed in sequestration of metal ions with special application in water softening.

Earlier studies[11-16] regarding the complexation of calcium, magnesium and other cations by Graham's salt in solution showed the formation of complexes with the formulae, $Na_2M_2P_6O_{18}$; these formulae were based on the then accepted hexameric nature of Graham's salt. Mehrotra[17] showed the versatility of the complexation tendencies of Graham's salt with a large number of cations, e g., alkali, alkaline and rare-earth metals, Be, Al, Zr, Th, Fe, Ni, Cu, Zn, Cd, Hg, Pb etc. Dhar and Mehrotra[18] synthesized a number of complexes of Graham's salt with calcium, strontium, barium, zinc, magnesium and lead in the form of glassy solids and assigned to them a formulation of the type $[Na_xM_{6-x/a}(PO_3)_6]$. Long chain polymeric character of Graham's salt was established with the help of several physicochemical techniques, viz. ultracentrifugation[19], dialysis[20], end-group titrations[21], viscosity measurements[22,23], light scattering[24], conductometry[25], electrolytic transference studies[26], chromatography[27,28], fractional precipitation[29], X-ray diffraction[30] etc. The above derivatives can therefore be interpreted to contain anions of the type $[Na_2M(PO_3)_6]_n^{2n-}$. This conclusion is supported by the findings of Wall and Doremus[31] based on their electrolytic transference studies also.

Later on, a large number of complex polymetaphosphate derivatives of Graham's salt of the composition $[Na_xM_{1-x/a}PO_3]_n$ [where M=K, Li, Ca, Ba, Zn, Cu or Fe(III) ; x=2/3, 1/2 or 1/3 and a is valency of metal M] were synthesised in the glassy form by Gupta[32]. These derivatives were found to be polymeric in nature similar to that of Graham's salt and exhibited polyelectrolytic behaviour[33-40].

The polymetaphosphate of more electropositive metal potassium $(KPO_3)_n$, known as potassium Kurrol's salt, has been synthesized by thermal dehydration of KH_2PO_4[41]. It differs from Graham's salt in being insoluble in water and having a different structure in the solid state[42]. Andress and Fischer[43] showed by X-ray studies that the anions of the compound consist of polymeric chains of $(PO_3)_n^{n-}$ units. Following the X-ray diffraction studies of Corbridge[44], Jost[45] has shown that crystals of $(KPO_3)_n$ are monoclinic belonging to the space group, $P_{2.1/a}$ with lattice constants as a=14.02Å, b=4.54Å, c=10.28Å and ∢=111.5°. The polyphosphate chain is of screw type and contains four PO_4 tetrahedra per period so that each potassium is surrounded by seven or eight oxygen atoms. According to Jost, the swelling in water or salt solutions and ion-exchange behaviour of $(KPO_3)_n$ can be attributed to relatively weak forces between 201 planes.

Keeping in view the solubility characteristics[46,47] and ion-exchange behaviour[48] of $(KPO_3)_n$, it was predicted by Mehrotra *et al*[49] that complex derivatives of the type $[K_xM_{1-x/a}PO_3]_n$ should behave differently and should probably be soluble in water. This conjecture has been confirmed by the synthesis of complex potassium polymetaphosphate glasses of mono and divalent metal ions. The complex derivatives of the composition $[K_xM_{1-x/a}PO_3]_n$ (where M=Li, Na, Ca, Sr, Ba, Zn, Cd, Cu, Ni or Pb ; x=2/3, 1/2 or 1/3 and a is valency of metal M) were synthesised, employing a fusion reaction (at 800°) of MO (M=bivalent metal), $(NH_4)_2HPO_4$ with KH_2PO_4. A few of the reactions have been followed by thermogravimetric and differential thermal analysis to throw light on the mechanism of the condensation reactions and the nature of the product formed. All these complex derivatives were obtained as clear, transparent glasses. The complex derivatives with x=2/3 were found to be easily soluble in water, but the solubility decreased with increasing ratio of the bivalent metal ion to potassium. The nature of these derivatives has been found to be similar to that of Graham's salt and other related compounds[50-52].

In view of the observed water soluble nature of these derivatives, it can be assumed that during dissolution of $(KPO_3)_n$ in salt solutions of electrolytes or in the suspension of cation exchange resin, formation of complex polymetaphosphate derivatives of the type synthesized by fusion technique takes place. This assumption has been verified in a different manner as well. When an aqueous suspension of potassium Kurrol's salt and bivalent metal polymetaphosphate $[M(PO_3)_2]_n$ in a molar ratio 4 : 1 is shaken together for a long time,

mutual dissolution of these two virtually insoluble derivatives takes place. On adding alcohol to the clear solutions thus obtained, precipitation of complex potassium polymetaphosphate derivatives of the composition $[K_4M(PO_3)_6.2H_2O]_n$ (M=Ca, Sr, Ba, Pb or Cd) takes place[55]. These reactions are thus corroborative of the parallelism envisaged by Thilo[46], between complexation reactions of polyphosphates and ion-exchange behaviour of synthetic ion-exchange resins.

Lithium polymetaphosphate $(LiPO_3)_n$ has a structure similar to diopside and thus differs from $(KPO_3)_n$ and $(CsPO_3)_n$. It is also obtained as a glassy product during thermal dehydration of lithium dihydrogen orthophosphate and is soluble in water like Graham's salt and cesium polymetaphosphate. The size of Li^+ cation is smaller than that of other alkali metal cations and it is also smaller than those of more electropositive bivalent metal ions. Therefore, its exchange by other cations in $(LiPO_3)_n$ should be comparatively lesser. The binding of alkali metal ions with polyphosphate chain has been investigated by Strauss *et al*[54]. The specific site bonding of cations on $(PO_3)_n^{n-}$ chain follows the order $Li^+ > Na^+ > K^+ > Cs^+ > Ca^+ > (CH_3)_4N^+$. Thus, it was expected that the complex derivativies of lithium polymetaphosphate should behave in a different manner. Hence, complex lithium polymetaphosphate derivatives of the composition $[Li_x M_{1-x/a}PO_3]_n$ (where M = Ca, Sr, Ba, Mg, Be, Cu, Ni, Cd, Zn, Pb etc. ; x=2/3, 1/2 and 1/3 and a is valency of metal M) were synthesized by Mehrotra and Oza[55]. All these derivatives were obtained as hygroscopic glassy solids. These were found to be water soluble, polymeric in nature and exhibited characteristic properties similar to that of Graham's salt and its complex derivatives[56-58].

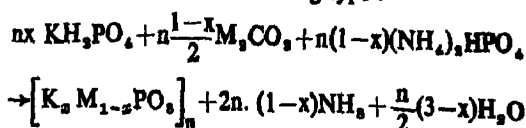
Cesium shows a close resemblance to potassium in its chemical properties. Cesium polymetaphosphate, $(CsPO_3)_n$, although isomorphous with potassium polymetaphosphate, is soluble in water unlike the latter. The course of thermal dehydration of KH_2PO_4 and CsH_2PO_4 has been studied with the help of complementary TGA, DTA and X-ray studies[59,60]. In both the systems $[MH_2PO_4$-$(MPO_3)_n]$ formation of trimetaphosphate is precluded and lower chain phosphates are directly converted to polymetaphosphates. In NaH_2PO_4-$(NaPO_3)_n$ system, a large number of condensed phosphate anions exists as intermediate products varying in nature with temperature and duration of heating. The water vapour pressure also plays an important role in stabilizing a particular product. Keeping this in view, cesium polymetaphosphate and its complex derivatives were synthesised[55] by fusion techniques. These derivatives of the composition $[Cs_x M_{1-x/a}PO_3]_n$ (where x=1, 2/3, 1/2 or 1/3 ; M=K, Ca, Sr, Zn, Cd or Pb and a is valency of metal M) are glassy solids except $(CsPO_3)_n$ which is obtained as an opaque mass. The investigations[61-63] of physicochemical properties of these derivatives haver evealed a close similarity with Gaham's salt and other complex alkali polymetaphosphates.

Among the polymetaphosphates of trivalent metal ions, synthesis of $[Fe(PO_3)_3]_n$ has been reported by Dyvoire[63] who obtained it by heating $Fe(H_2PO_4)_3$ to a temperature greater than 850°. The reaction of $FeCl_3$ with $(NaPO_3)_n$ in solution was investigated by Mehrotra and Gupta[40]. It was established with the help of *p*H-metric and conductometric studies that compounds of the composition $[Fe_2(OH)_3(PO_3)_3]_n$ is formed instead of the expected $[Fe(PO_3)_3]_n$ derivative. The simple Fe(III) polymetaphosphate or complex sodium-iron polymetaphosphate could not be synthesized by fusion technique. Lanthanum and other lanthanide elements have electronegativity values in the range of alkaline earth metals. Their characteristic oxidation state is +3. It is worthwhile to mention here that polymetaphosphates of trivalent lanthanides can not be prepared by thermal dehydration of their acid orthophosphates. The complexation reactions of lanthanides with some oligophosphates have been investigated by some Russian workers[64-66]. However, their long chain polyphosphates have not been synthesised. Hence, the reactions of lanthanum, yttrium and cerium(III) nitrates with alkali metal polymetaphosphates have been investigated by *p*H-metric and conductometric technique. On the basis of results obtained from these studies polymetaphosphate derivatives of the composition $[M(PO_3)_3]_n$ could be obtained as precipitates. A soluble complex derivative of the composition $[Na_{1/2}La_{1/6}(PO_3)]_n$ could also be obtained by precipitation technique for the first time, and its polymeric as well as polyelectrolytic characteristics have been investigated.

Experimental

(*A*) *Synthesis* :

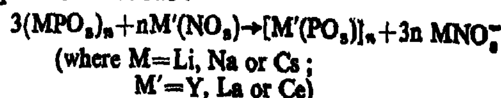
(i) *Preparation of complex polymetaphosphates of potassium with lithium or cesium* : The above complex glasses were synthesized at 800° by the fusion reactions of the following type :



$$nx\,KH_2PO_4 + n\frac{1-x}{2}M_2CO_3 + n(1-x)(NH_4)_2HPO_4 \rightarrow \left[K_x M_{1-x}PO_3\right]_n + 2n.(1-x)NH_3 + \frac{n}{2}(3-x)H_2O$$

(where M=Li or Cs ; x=2/3, 1/2 or 1/3)

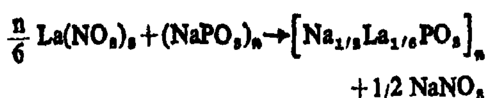
(ii) *Synthesis of polymetaphosphates of yttrium lanthanum and cerium* : When solutions of lithium, sodium or cesium polymetaphosphates, $(MPO_3)_n$, synthesized as described earlier[52,49,55], were mixed with metal salt solutions in the molar ratio 3 : 1 precipitates were obtained. The reactions could be expressed as follows :



$$3(MPO_3)_n + nM'(NO_3) \rightarrow [M'(PO_3)]_n + 3n\,MNO_3^-$$

(where M=Li, Na or Cs ;
M'=Y, La or Ce)

(iii) *Synthesis of the complex derivative* $[Na_{1/2}$-$La_{1/6}PO_3]_n$: This complex derivative was separated by the addition of alcohol to a clear solution obtained by mixing sodium polymetaphosphate solution and lanthanum nitrate solution in the molar ratio 6 : 1.



$$\frac{n}{6}\,La(NO_3)_3 + (NaPO_3)_n \rightarrow \left[Na_{1/2}La_{1/6}PO_3\right]_n + 1/2\,NaNO_3$$

The precipitate thus obtained was dried at reduced pressure at room temperature

All the above derivatives (I-III) synthesized during the present investigations were analysed for metal and phosphorus contents (Table 1).

III. *Paper chromatographic studies* were carried out on a Whatman No. 1 chromatographic filter paper employing Ebel's[69] acidic solvent. R_f and R_g values for different polymer samples were recorded (Table 2).

IV. *pH-metric titrations* of yttrium, lanthanum and cerium(III) salt solutions with alkali polymetaphosphate $(MPO_3)_n$ solutions were performed employing a 'Cambridge' bench type *p*H-meter and glass and calomel electrodes. Fig. 2 shows the *p*H-titrations of $La(NO_3)_3$ with alkali polymetaphosphate solutions.

TABLE 1—ANALYSIS OF SIMPLE AND COMPLEX POLYMETAPHOSPHATE DERIVATIVES

Formula of the compd. and mode of symthesis	% metal M'		% metal M"		% Phos.	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
Synthesized by fusion at 800°						
$[K_{2/3}Li_{1/3}PO_3]_n$	23.71	24.27	2 11	2.15	28.71	28.84
$[K_{1/2}Li_{1/2}PO_3]_n$	19.13	19.17	3.38	3 40	30.33	30.38
$[K_{1/3}Li_{2/3}PO_3]_n$	13.70	13.76	4.77	4.79	31.99	32.06
$[Cs_{2/3}K_{1/3}PO_3]_n$	—	—	7.30	7.22	17.20	17.16
$[K_{1/2}Ca_{1/4}PO_3]_n$	17.03	17.08	13 86	13.89	27.03	27.08
Obtained by precipitation from clear solution						
$[Na_{1/2}La_{1/6}PO_3\,H_2O]_n$	—	—	24 05	23.55	17.88	17.59
Obtained as precipitates						
$[La(PO_3)_3]_n$ dried at 135°	27 10	26 98	—	—	24.57	24.73
$[Y(PO_3)_3.3H_2O]_n$ dried over pump	23 52	23 41	—	—	24 35	24.46
$[Ce(PO_3)_3.3H_2O]_n$ dried over pump	32.37	32.50	—	—	21.29	21.56

(B) *Physicochemical properties of the new derivatives* :

(I) *Number average molecular weights* of all these derivatives were determined by end-group titration technique[60,67]. As suggested by Gustavsson and Larrson[68], a dilute hydrochloric acid solution was added to bring the *p*H of the polymer solution upto 3.0 to 3.5. On titration with sodium hydroxide solution, two breaks were obtained at *p*H values around 4 and 9 and from this titre value, the number average molecular weights (Mn) of the polymer can be calculated by the formula.

$$Mn = \frac{2000 \times \text{wt of polymer dissolved in solution}}{\text{ml of } N \text{ NaOH required}}$$

The Mn values are recorded in Table 2.

TABLE 2—R_f AND R_g VALUES FOR COMPLEX ALKALI POLYMETAPHOSPHATE DERIVATIVES IN EBEL'S ACIDIC SOLVENT (FLOW TIME -20 hr) ALONGWITH THEIR NUMBER AVERAGE MOLECULAR WEIGHTS (Mn)

Formula of the compound	R_f	R_g	Mn
$[K_{2/3}Li_{1/3}PO_3]_n$	0.10	0.14	4000
$[K_{1/2}Li_{1/2}PO_3]_n$	0 09	0.12	5000
$[K_{1/3}Li_{2/3}PO_3]_n$	0.10	0 14	4500
$[K_{1/2}Ca_{1/4}PO_3]_n$	0.14	0.20	3300
$[Cs_{2/3}K_{1/3}PO_3]_n$	0.030	0.042	12000
$[Na_{1/2}La_{1/6}PO_3]_n$	0 08	0 12	7000
$(NaPO_3)_n$	0.064	0.084	8000
$(LiPO_3)_n$	0 068	0.090	6000
$(CsPO_3)_n$	0 027	0.039	12000

II. *Conductance measurements* at different formal concentration of the polymer solution were carried out on a RLC Tesla bridge employing a Philips Conductivity Cell (cell factor 1.49). The plots of equivalent conductance versus square root of concentrations are shown in Fig. 1.

Conductometric titrations of yttrium, lanthanum and cerium(III) salt solutions were also performed on RLC Tesla bridge, employing a 'Philips' conductivity cell. Fig. 3 shows the plot of specific conductance versus moles of alkalipolymetaphosphate added during the titration of lanthanum nitrate with alkalipolyphosphates.

Results and Discussion

General: Unlike potassium Kurrol's salt $(KPO_3)_n$, the complex polymetaphosphate derivatives $[K_xLi_{1-x}PO_3]_n$ (where x=2/3, 1/2 or 1/3) were obtained as clear transparent glasses and were found to be soluble in water. This is expected keeping in view the ion-exchange behaviour of alkali polymetaphosphates[48]. Similar observations have been reported earlier by Mehrotra and Vyas during their studies on complex potassium polymetaphosphate derivatives[50-55]. However, in the case of complex cesium polymetaphosphate derivatives containing potassium and cesium it has been found that only one derivative i.e. $[Cs_{2/3}K_{1/3}PO_3]_n$ was found to be soluble in water whereas the other two derivatives i. e. $[Cs_{1/2}K_{1/2}PO_3]_n$ and $[Cs_{1/3}K_{2/3}PO_3]_n$ did not dissolve in water even after prolonged shaking. Thus, with the increase in ratio of potassium in the polyphosphate chain the solubility diminishes. In the case of complex lithium derivatives of potassium Kurrol's salt the solubility of the compounds in all mole ratios could be ascribed to effective ion-exchange of K^+ by small Li^+ ions, whereas larger K^+ ions are not able to do so when the ratio K^+/Cs^+ increases. Ohashi and coworkers[69]

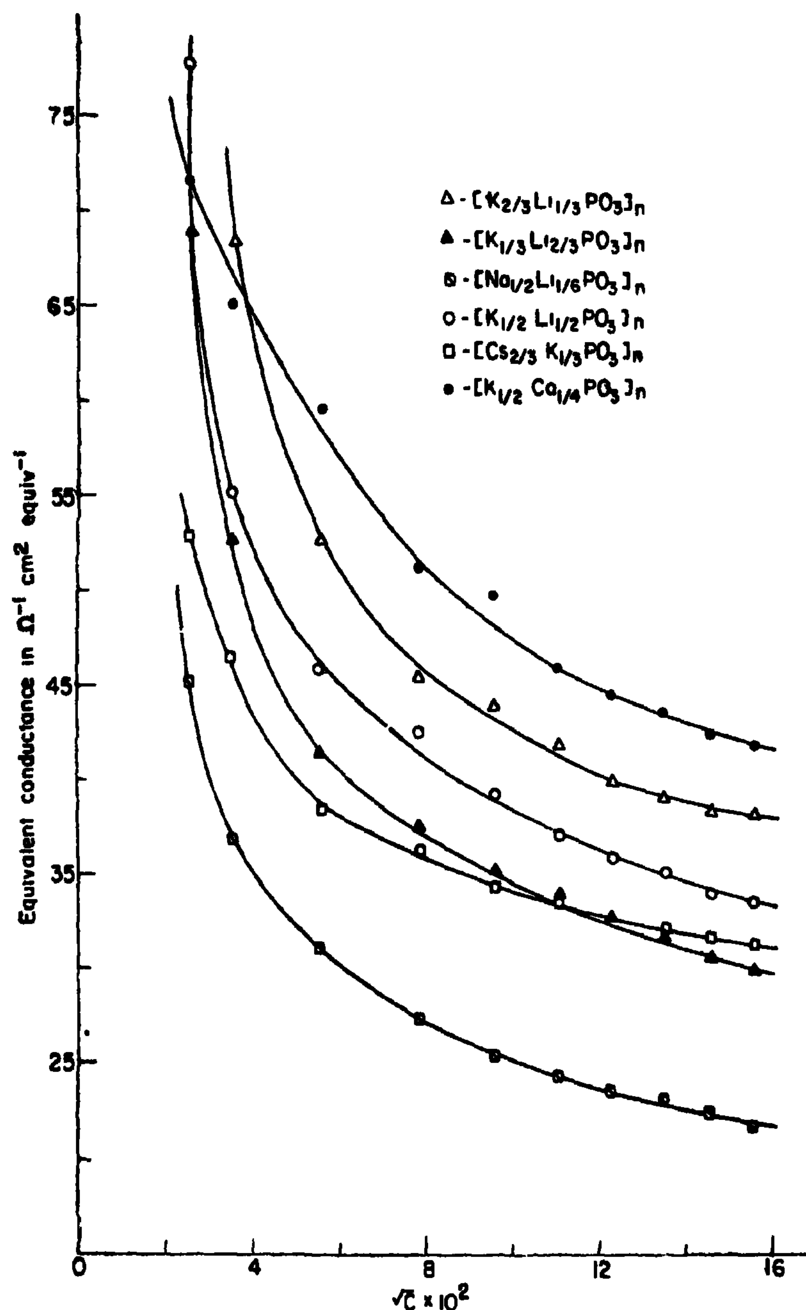
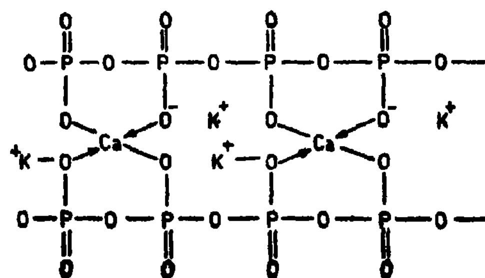


Fig 1. Plot of equivalent conductance versus square root of concentration.

have also observed that in aqueous solutions of bivalent metal ions the exchange of K^+ can occur to the extent of 82-94% in the potassium Kurrol's salt. The insolubility of the complex polymetaphosphate derivatives of barium and strontium of the composition $[K_{1/3}M_{1/3}PO_3]_n$ and $[K_{1/2}M_{1/4}PO_3)_n$ (M=Ba or Sr) suggests that exchange of K^+ ion by Ba^{2+} and Sr^{2+} ions can occur only to the extent of less than 50%. The exchange of K^+ ion by Ca^{2+} in $(KPO_3)_n$ can occur to the extent of 50% as evident from the solubility of the complex derivative $(K_{1/2}Ca_{1/4}PO_3)_n$. The above behaviour seems plausible in view of the formation of dianionic chains of the type given below, as suggest Eisenberg[70].



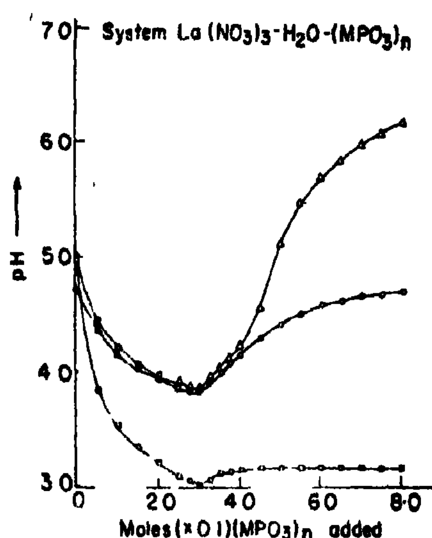


Fig. 2. 25 ml $M/250$ $La(NO_3)_3$ titrated pH-metrically against $M/100[NaPO_3]_n$, □$[LiPO_3]_n$ and △$[CsPO_3]_n$.

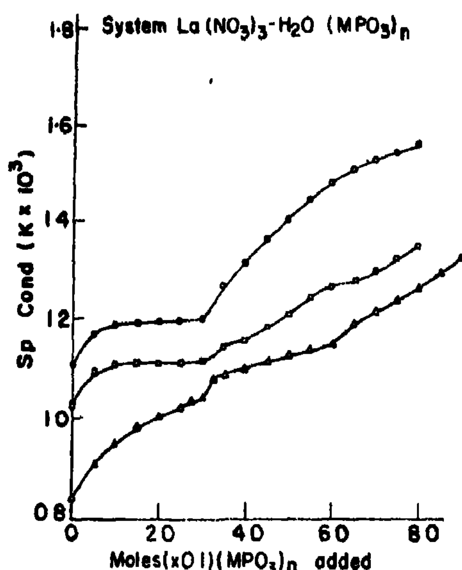


Fig 3 25ml $M/250$ $La(NO_3)_3$ titrated conductometrically against $M/100[NaPO_3]_n$, □$[LiPO_3]_n$ and △$[CsPO_3]_n$.

The formation of such cross linked structures might result in increasing the lattice force making the exchange of ions difficult.

Complexation reactions of $(MPO_3)_n$ *with* La^{3+}, Ce^{3+} *and* Y^{3+}: Synthesis of simple or complex polymetaphosphate derivatives of lanthanum and other lanthanides was tried by fusion method but a melt could not be obtained even at a temperature of 1100°. During the pH-metric and conductometric titrations of Y^{3+}, La^{3+} and Ce^{3+} salt solutions with $(MPO_3)_n$ solutions (M=Li, Na or Cs) it was found that precipitation occurs till Ln^{3+} : P ratio equals 1 : 3. At this stage an inflection can be seen in the titration curves (Figs. 2, 3). Hence the compounds $[Ln(PO_3)_3]_n$ (Ln=Y^{3+}, La^{3+} or Ce^{3+}) were isolated by mixing $La(NO_3)_3$ solutions and $(MPO_3)_n$ solutions (where M=Li, Na or Cs) in the molar ratio 1 : 3. The precipitates obtained were washed with water, dried and analysed for metal and phosphorus. The analyses (Table 1) corresponds to the above composition.

During the above titration, it can be observed that the precipitate starts dissolving on addition of excess (>3 moles) of $(MPO_3)_n$ solution. Thus, in the titration of $La(NO_3)_3$ with $(NaPO_3)_n$ a clear solution was obtained at La : P ratio of 1 : 6. This indicated the formation of a complex derivative of the composition $[Na_{1/2}La_{1/6}PO_3]_n$. It was isolated by mixing together $La(NO_3)_3$ solution and $(NaPO_3)_n$ solution in molar ratio 1 : 6 and adding ethanol. The precipitate obtained was washed with alcohol and dried under reduced pressure. It was analysed for lanthanum and phosphorus and the composition was found to be $[Na_{1/2}La_{1/6}PO_3.H_2O]_n$ (Table 1).

Number average molecular weights (Mn) of complex polymetaphosphate: The number average molecular weight (Mn) data (Table 2) suggest polymeric nature of the complex polymetaphosphate synthesized as above. The Mn values of complex potassium lithium polymetaphosphate were found to be in the range of 4000-5000 while that of $[Cs_{2/3}K_{1/3}PO_3]_n$ was found to be 12000. It has been reported that most of the polymetaphosphate derivatives of lithium have molecular weights in the range 3500-5000. Cesium polymetaphosphate and its complex derivatives have molecular weights (Mn) in the range 10000-12000. These data suggest that in presence of small strongly binding counter ions, a greater degree of cross linking through the formation of dianionic chain results and hence these derivatives are characterized by low Mn values. Eisenberg[20] in a study of the polyphosphate polymers, homopolymers containing Li^+, Na^+, Ca^{2+}, Ba^{2+}, Zn^{2+} and Cd^{2+} and counter ion polymeric systems such as Na^+-La^{3+}, Na^+-Ca^{2+}, Na^+-K^+, K^+-Li^+ in the glass transition range revealed that the diionic chains possess cross linking character as compared to those in which the repeat units contain only one type of cation. The molecular weights of $[Na_{1/2}La_{1/6}PO_3]_n$ sample obtained by precipitation technique was found to be in the range of 7000, whereas the molecular weight of the Graham's salt sample from which it was synthesized was around 10000. It, however, indicates that the compound possesses polymeric nature similar to that of Graham's salt.

Polyelectrolytic character: The conductance of complex polymetaphosphate solutions are generally in the same range (within 15-20%) as that of the simple alkalipolymetaphosphates from which these derivatives are obtained. The equivalent conductance at different formal concentrations are given in Table 2. This indicates that the mobilities of the anions are not markedly affected by the complete or partial substitution of alkali metal by other metal ions. This is in conformity with the structures suggested by Mehrotra[17]. Wall and Doremus[21] had also shown in 1954 that the ionic mobilities of polyanions in the solutions of $(NaPO_3)_n$ and

$(Na_{1/2}Sr_{1/4}PO_3)_n$ are of the same order. The plot of equivalent conductance ,λ, versus square root of concentration ,$\sqrt{C}$, (Fig. 1) is typical of polyelectrolytes i.e., has parabolic shape. Thus, the conductance measurements demonstrate the polyelectrolytic nature of these complex derivatives.

Paper chromatographic studies : The paper chromatographic studies of the complex polymetaphosphate derivatives were carried out in acidic solvents. The R_f and R_g values are recorded in Table 2. From these values it can be seen that the R_f and R_g values for the complex compounds are in close agreement with those for Graham's salt and other alkalipolyphosphates and are different from those reported for trimetaphosphates and other lower phosphates. This indicates a long chain polymeric character for these derivatives just similar to that of Graham's salt. A very weak spot due to the trimetaphosphates is also observed which is probably due to the hydrolysis of the polymetaphosphates during the course of the flow of the solvent. Trailing effect was observed in some cases but the R_f and R_g values could be calculated without much difficulty.

Hence, it is clear from these studies that the complex polymetaphosphate derivatives containing more than one electro positive metals have almost all the characteristics similar to that observed for Graham's salt and other related compounds. It can thus be concluded that all these derivatives, although containing different metal combinations and synthesized in different manners, heve properties similar to that for Graham's salt and other long chain polyphosphates.

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Heterogeneous Ion-Selective Electrodes Based on Electroneutral Ion-Carriers : Barium(II) and Nickel(II) Electrodes

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Heterogeneous barium(II) and nickel(II) selective electrodes based on electroneutral complexes, formed from cyclic ligands 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene for Ba(II) ; and 1,4,8,11-tetraazocyclotetradecane for Ni(II) have been described. The electrodes have short response time, are mechanically stable and give fairly constant potentials within a wide range of *p*H. The selectivity coefficients, determined by mixed solution method, for a number of cations are found to be less than unity for both the electrodes. The electrodes have been found to be satisfactory in electrometric titrations. Using the Ni(II)-electrode, the stability constant of 1 : 1 nickel-sulphosalicylic acid complex was determined, log K_1 = 9 07 (30°, $I \approx 0.005$).

ION-selective electrodes based on liquid membranes are well known[1-3]. These membranes contain either dissolved ion-exchangers or electroneutral ion-carriers. In the latter case, the membrane consists of a suitable inert organic solvent with a dissolved macrocyclic substance which may be an antibiotic, a macrotetrolide, a cyclic polyether or a macromolecular acyclic compound[4]. The structure of the macrocyclic substance favours the formation of a polar cavity in which a specific ion can be enclosed because of ion-dipole interactions. However, the construction of such an electrode poses mechanical problems[5]. The liquid phase containing the electroactive material must be immiscible with the test solution, the loss of the liquid by evaporation should be minimum, and the concentration of the electroactive substance in the membrane should remain uniformly constant. To overcome these difficulties, it was thought worthwhile to prepare a heterogeneous membrane with the electroneutral complex held in a fixed matrix, thus overcoming the problems encountered with a liquid membrane. An attempt has therefore been made to construct electrodes for Ba(II) and Ni(II), using the metal complex as well as the ligand alone, as electroactive materials For Ba(II) ion, the polyether, 2, 3-benzo-1,4,7,10, 13-pentaoxacyclopentadeca-2-ene (benzo-15-crown-5) and for Ni(II) ion, 1,4,8,11-tetraazocyclotetradecane (cyclam-14) have been employed as ligand. The electrodes are similar to the solid state ones.

Experimental

Preparation of Ba(II) complex : The complex of Ba(II) with benzo-15-crown-5 was prepared by the method of Pederson[6]. To a solution of 400 mg of $BaCl_2.2H_2O$ (BDH AnalaR) in 5 ml methanol, 900 mg of the crown ether was added and dissolved by stirring at room temperature. The solution was allowed to evaporate at room temperature (~30°) for several days, till the complex was obtained in the form of a slurry This was dried by pressing between filter papers, washed with a small quantity of methanol and dried again at room temperature.

Preparation of membrane · In order to provide mechanical strength to liquid membranes, a layer of PVC to support the liquid has sometime been adopted[7,8]. Problems like immiscibility of liquid and solution, loss by evaporation etc. still remain. Hence in the present studies epoxy resin (Araldite, Ciba India Ltd.) was employed to obtain the membranes, which gave well defined interface and enhanced the mechanical resistance to stirring and pressure effects. The membranes were solid state and were obtained as described elsewhere[9].

The following membranes (master disc) were obtained by mixing the electroactive materials and Araldite :

(i) 100 mg of benzo-15-crown-5+150 mg of Araldite.

(ii) 100 mg of the barium complex+150 mg of Araldite.

(iii) 100 mg each of cyclam-14 and Araldite.

(iv) 100 mg each of nickel complex and Araldite

The electrodes using the above membranes were called, I, II, III and IV, respectively.

Preparation of electrode . To prepare the electrodes, a piece of membrane ~1 cm in diameter was cut out from the respective master disc and fixed at one end of a 10 cm long glass tube (inner diam ~ 8 mm) with Araldite. In the first two electrodes the internal solution kept was 0.1 mol dm^{-3} $BaCl_2$, while in the other two it was $Ni(NO_3)_2$. A saturated calomel electrode (SCE) served for electrical contact.

Instruments : A digital *p*H-meter (Systronics, Model 335) with a second SCE as reference was used for electrode potential measurements. Measurements were made at 30±1°.

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Results and Discussion

Electrode response : The response of electrodes I and II in solutions of $BaCl_2$ of different concentrations was followed with the aid of the *p*H-meter. Initially, electrode I gave linear response in the concentration range $1\times10^{-1}-1\times10^{-4}$ mol dm^{-3} of $BaCl_2$ and the slope was *ca* 43 mV per decade change in concentration. However, the electrode was unsuitable for work, since with passage of time, it gave erratic response and the linearity was lost.

Electrode II gave linear response down to 5×10^{-5} mol dm^{-3} with a slope value 46 in the first week, but the value changed to 38 mV per decade change in concentration in the second week (Fig. 1) which remained constant for atleast 5 weeks. The analytical range of the electrode could be extended down to 5×10^{-6}mol dm^{-3} of Ba(II). The electrode gave excellent response also in aqueous ethanol medium (Fig. 1).

The response of electrodes III and IV were

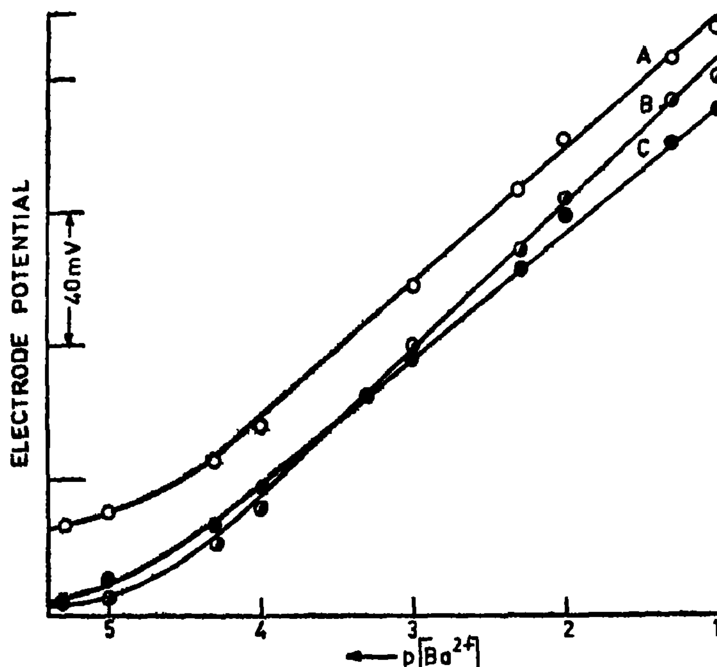


Fig 1. Calibration curve for electrode II, A : 60% ethanol solution ; B : 40% ethanol solution ; C : aqueous solution.

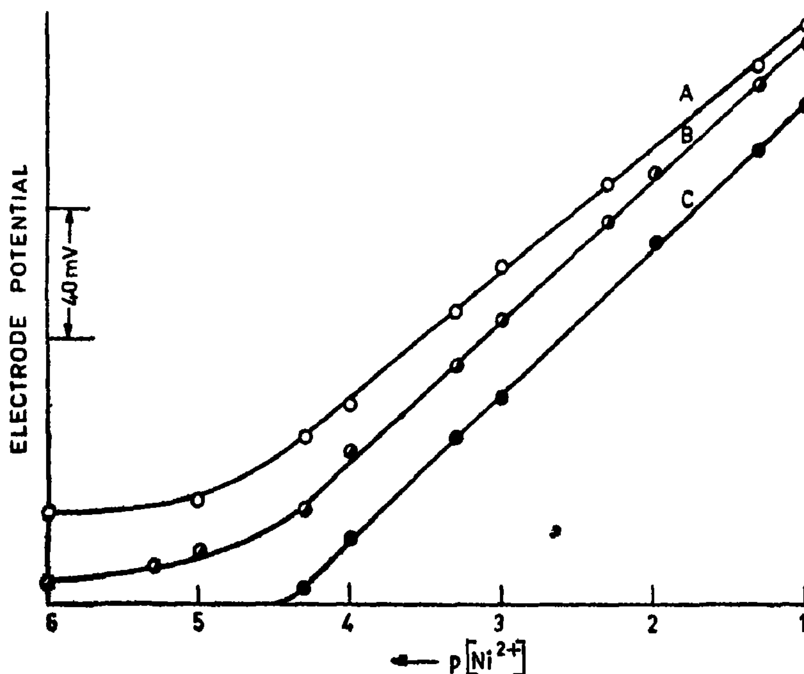


Fig. 2. Calibration curve for electrode IV, A : 40% ethanol solution ; B : aqueous solution ; C : 20% DMF solution.

recorded at different concentrations of $Ni(NO_3)_2$. Electrode III failed to give uniformly a linear response and was not considered useful. During the first four days of its preparation, electrode IV showed linear response down a concentration of 1×10^{-4} mol dm^{-3} of Ni(II) with a slope of 44 mV per decade change in concentration. In the second week, however, a linear response down to 5×10^{-5} mol dm^{-3} of Ni(II) with 39 as slope value was observed (Fig. 2). Though the value of 39 is slightly higher than the expected Nernstian value in the case of a bivalent ion, the value did not change atleast for 8 weeks. Linear response was also observed in 40% aqueous-ethanol and in 20% aqueous-dimethylformamide (Fig. 2).

Both in case of electrodes II and IV, 80% of the total potential was reached within 20 seconds when concentration of $BaCl_2$ or $Ni(NO_3)_2$ was varied from 0.01 to 0.001 mol dm^{-3}. After 40 seconds, the potential got stabilised and remained constant thereafter.

Effect of pH : The potential remained constant in the *p*H range 3.5—8.0 for both electrodes II and IV (Fig. 3). This indicates the working ranges of *p*H for the electrodes.

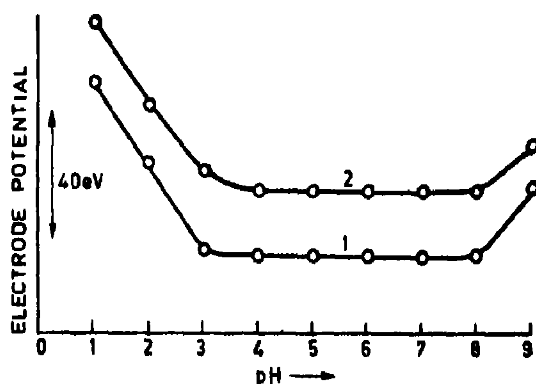


Fig 3. Potential—*p*H diagram for electrodes II (curve 1) and IV (curve 2).

Interference by ions : The cationic interferences due to other ions were studied by the determination of selectivity coefficients by mixed solution method[6,7]. The electrode potentials were recorded in mixed solutions having a fixed concentration of interferant, B (1×10^{-3} mol dm^{-3}) and varying concentrations (1×10^{-1} to 1×10^{-6} mol dm^{-3}) of either $BaCl_2$ or $Ni(NO_3)_2$ (M). The selectivity coefficients were calculated from the plot of potential of electrodes system vs concentration in the usual manner [6,7,10] (Table 1). The values of selectivity coefficients are less than unity in all the cases. However, for electrode II, the value for Mg(II) and for electrode IV, the value for Co(II) approach unity. The value <1 suggests[7] that the electrode responds selectively to Ba(II) or Ni(II) in presence of a number of other ions.

The calibration curves were drawn by taking measurements in two different salts of Ba(II) or Ni(II) ion. It was found that in the cases of both Ba(II) and Ni(II) electrodes, chloride and nitrate solutions gave identical curves. Consequently either of the solutions can be used for calibration purposes.

TABLE 1—SELECTIVITY COEFFICIENTS ($K_{M,B}$) OF ELECTRODES II AND IV IN MIXED SOLUTIONS AT 30±1°

Foreign ion	Selectivity coefficient	
	Electrode II	Electrode IV
K^+	0.80	(*a*)
Na^+	0.41	0.08
NH_4^+	0.56	(*a*)
Mg^{2+}	0.90	0.38
Ca^{2+}	0.62	0.31
Sr^{2+}	0.50	(*a*)
Mn^{2+}	(*a*)	0.65
Co^{2+}	(*a*)	0.95
Cu^{2+}	(*a*)	0.62
Zn^{2+}	0.75	0.42
Cr^{3+}	(*a*)	0.02
Al^{3+}	(*a*)	0.04

(*a*) Not determined.

Applications : The utility of electrodes II and IV in analytical studies was established by electrometric titrations of Ba^{2+} against SO_4^{2-} using electrode II, and Ni^{2+} against EDTA using electrode IV, both of which gave satisfactory results.

Ion-selective electrodes have been used in the direct determination of the free metal ion concentration in metal-ligand equilibria[10-13]. The stability constant of the complex in solution can be evaluated therefrom. The stability constant of 1 : 1 Ni(II)-sulphosalicylic acid (SSA) complex has been determined to further illustrate the use of electrode IV.

SSA has three ionizable protons, the proton from the sulphonic acid group dissociates completely[13] at *p*H~1, and consequently, in aqueous solution, the ligand exists as H_2L^-. The metal-ligand equilibria are (charges are omitted) :



$$M+H_2L \rightleftharpoons ML+2H \quad \ldots\ 1$$
$$ML+H_2L \rightleftharpoons ML_2+2H \quad \ldots\ 2$$

Eq. 1 represents the formation of 1 : 1 species and the total metal ion concentration is given by

$$M^o=[M^{2+}]+[ML^-] \quad \ldots\ 3$$

from which K_1 works out to be

$$K_1=\frac{\left\{\frac{M^o}{[Ni^{2+}]}-1\right\}}{[L^{3-}]} \quad \ldots\ 4$$

where, $[L^{3-}]$ is the free ligand concentration and can be evaluated from the expression[14]

$$[L^{3-}]=\frac{L^o-\{M^o-[Ni^{2+}]\}}{\phi} \quad \ldots\ 5$$

In eq. 5, L^o is the total ligand concentration and ϕ is given by

$$\phi=1+\frac{[H]}{K_3^H}+\frac{[H]^2}{K_2^H\ K_3^H} \quad \ldots\ 6$$

K_2^H and K_3^H are the equilibrium constants corresponding to the dissociation of carboxyl and phenolic hydrogens respectively, and [H] is the hydrogen ion concentration.

A series of solutions were prepared in which the concentrations of metal and ligand were kept constant, but pH was varied in the range 4.5—5.3, where only the 1 : 1 species are formed[15]. The electrode potential of each solution was measured and the corresponding values of [Ni^{2+}] were obtained from the calibration curve. The dissociation constant (at I=~0.005) being known[14], the free ligand concentration and therefrom the value of log K_1 was calculated to be 9.07. The value agreed with that determined by Bjerrum-Calvin titration technique[14].

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Correlation of Electrode Behaviour and Spectral Properties of Some Mixed-Ligand Complexes of Copper(II)

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Analyses of the electrode behaviour with regard to half-wave potential '$E_{\frac{1}{2}}$', formal rate constant 'K_f', activation energy of rearrangement Q_e and activation energy of diffusion, Q_D *vis-a-vis* spectral behaviour of mixed-ligand complexes of Cu(II) with 2,2'-bipyridyl and 1,10-phenanthroline as primary ligands and some aliphatic, aromatic, amino acids and phenols as secondary ligands have been made In aqueous potassium nitrate solution, the complexes containing bipyridyl as primary ligand give two-electron, single-step reduction wave while the complexes containing phenanthroline as primary ligand give two step electro-reduction wave at dme All the systems are observed to be diffusion controlled and irreversible. A correlation of electrode behaviour with the spectral parameters has been attempted *It has been observed that the half-wave potential shifts towards more negative side as the ligand field shifts towards higher energy side* The rate constant shows a decreasing trend in conformity with this. A possible mechanism of electron transfer has been suggested on the basis of orientation of orbitals towards the electrode. The activation energy of diffusion shows a direct relationship with the energy difference between binary and ternary complexes in a particular series

IT is being increasingly realized that transition metal complexes behave characteristically at the dropping mercury electrode yielding information about the lowest vacant orbital. Considering that information about the highest occupied orbital may be gained from spectral behaviour of such a system, it should be possible to correlate redox properties of coordination compounds with their spectral properties. Following this idea, attempts[1-9] have been made in the last decade to seek correlation of the spectral characteristics *vis-a-vis* electrode behaviour of coordination compounds with some success. Work on mixed-ligand complexes, however, is very scanty.

In the work embodied in the present communication, such a correlation has been attempted by studying electrode behaviour of some mixed-ligand complexes of a biologically important transition metal like copper and important ligands such as 2, 2'-bipyridyl $(C_5H_4N)_2$ and 1, 10-phenanthroline $(C_{12}H_8N_2)$ as primary ligands and aliphatic acids, aromatic acids, amino acids and phenols as secondary ligands. Such mixed-ligand complexes are likely to be important as models for metallo-enzyme substrate complexes and also as components of the multi-metal-multi-ligand systems in biological fluids. The complexes studied are [Cu(bip)L] and [Cu(phen)L] in 1 : 1 : 1 and 1 : 2 : 1 ratio, where bip stands for 2, 2'-bipyridyl, phen stands for 1,10-phenanthroline and L stands for aliphatic acids [formic acid, HCOOH ; oxalic acid, $(COOH)_2$; tartaric acid, $(CH\ OHCOOH)_2$; citric acid, $(CH_2COOH)_2C(OH)COOH$; succinic acid, $(CH_2COOH)_2$ abbreviated as (For), (Ox), (Tar), (Cit), (Suc) respectively], aromatic acids [benzoic acid, (C_6H_5COOH) ; phthalic acid, $C_6H_4(COOH)_2$; salicylic acid, $C_6H_4OH.COOH$; mandelic acid, $C_6H_5CH(OH).COOH$; gallic acid, $C_6H_2(OH)_3$-COOH abbreviated as (Ben), (Ph), (Sal), (Man), (Gal) respectively], amino acids [glycine, $(NH_2CH_2$-$COOH)$; valine, $(CH_3)_2CHCH(NH_2)COOH$; serine $HOCH_2CH(NH_2)COOH$; leucine $(CH_3)_2$ $CHCH_2CH(NH_2)COOH$ abbreviated as (Gly), (Val), (Ser), (Leu) respectively], and phenols [resorcinol, $C_6H_4(OH)_2$ and catechol, $C_6H_4(OH)_2$ abbreviated as (Res) and (Cat) respectively] Spectral studies[10-12] on these complexes reveal that they are having distorted octahedral stereo-chemistry in water. A probable mechanism of electron transfer from the electrode to the complex depolarizer, based on the above correlation, has been attempted for these series of complexes.

Studies in uv region of these ternary complexes have also been made with a view to observe metal-ligand and ligand-ligand interaction. The polarographic behaviour has been compared with the charge transfer transitions.

Experimental

Spectra of these complexes have been recorded on a Beckmann double beam with auto recording spectrophotometer Model 26, in the range of 400 to 900 nm for visible and 200 to 400 nm for uv regions.

Polarographic measurements have been made with a manual polarographic circuit recommended by Kolthoff and Lingane having Leeds and Northrup potentiometer and galvanometer assembly. All the potentials are measured against a Hume and Harris saturated calomel electrode (SCE). For the polarographic study, potassium nitrate of AnalaR grade has been used as a supporting electrolyte. Oxygen is removed from the solution with a stream

of oxygen-free nitrogen. Resistance of the system is measured by an ac wheatstone bridge. The resistance was between 700-800Ω. The characteristic of dme in aqueous medium (open circuit) has been determined for at least three heights. Result of one set is given below :

h=40 cm, m=2.43 mgs^{-1}, t=3.23 sec, $m^{2/3}t^{1/6}$ =2.198 $mg^{2/3}$ $sec^{-1/2}$.

All solutions are prepared in aqueous medium. 20 ml of total solution has been taken in the polarographic cell in each case.

Results

The polarographic characteristics of the systems studied here are described in detail elsewhere[13]. In 0.5*M* aqueous KNO_3 as supporting electrolyte, all these mixed-ligand complexes of bipyridyl produce single well-defined polarographic waves, except the complexes [Cu(bip)Gal], [Cu(bip)Leu] and [Cu(bip)-Cat] where double waves are observed. In the mixed ligand complexes of phenanthroline, double waves are obtained in every case. The nature of double wave can be explained on the basis of adsorption. All these electrode processes are found to be diffusion-controlled. The value of n, the number of electrons transferred, thus obtained from the Ilkovic equation was nearly equal to two for each of the bipyridyl mixed-ligand complexes except for the above three complexes as also the phenanthroline complexes where the value of n is lower. All the complexes are observed to undergo irreversible electroreduction under the present experimental conditions. Oldham and Parry's equation[14] has been used to calculate the formal rate constant K_f and transfer coefficient value. The activation energy Q_e and the activation energy of diffusion Q_D have been calculated using the equation given by Vlček[15]. The values of $E_{1/2}$, K_f, Q_D and Q_e for these systems are given in Tables 1, 2, 3 and 4.

All the mixed ligand complexes give one spectral band with ν_{max} in the range of 600-700 nm as shown in Tables 1-4, for both the complexes of the type [Cu(bip)L] and [Cu(phen)L]. Data show the energy difference of the binary(1 : 1) and the ternary (1 : 1 : 1) and (1 : 2 : 1) complexes. Changes take place in the energy of ternary complexes according to their ligand-field strength. Perusal of data shows that in this series, complexex [Cu(bip)Ox], [Cu(bip)Ben], [Cu(bip)Val] and [Cu(phen)Ox] give maximum absorption value (ν_{max}). This leads to the conclusion that these secondary ligands (oxalic acid, benzoic acid and valine) have a very strong ligand-field strength. However, in case of complexes of the type (1 : 2 : 1), there is no marked energy difference in the binary (1 : 2) and the ternary (1 : 2 : 1) complexes. The ν_{max} values of ternary complexes [Cu(bip)Ox] and [Cu(phen)Ox] (1 : 2 : 1) have high energy values in comparison to the other ternary complexes. One may conclude that oxalic acid is a very strong ligand in comparison to the other ligands used have which can affect the energy of the complex (1 : 2 : 1) while in others, energy is not affected by the addition of secondary ligand. Comparison of the polarographic and spectral data (visible) are given in Tables 1-4.

Spectral data of mixed ligand complexes of copper(II) in the uv range are given in Tables 5 and 6 including data on binary complexes [Cu(bip)] and [Cu)phen)] in 1 : 1 and of primary ligands alone.

Two bands are obtained in the case of bipyridyl and phenanthroline which further split in binary and ternary complexes.

TABLE 1—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : BIPYRIDYL WITH SECONDARY LIGANDS 1:1:1

Complex	$E_{\frac{1}{2}}$ V vs SCE	Formal Rate Constant "K_f" 1×10^{-4} cm sec^{-1}	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	Activation energies Q_D Kcal	Q_e Kcal
Cu : Bipyridyl	−0 1065	1.557×10^{-1}	14285	0	3 25	6.72
Cu : bip : Formic acid	−0.0980	1 642	14285	0	2 32	5.82
Cu : bip : Oxalic acid	−0 1100	1.562	15625	−1340	3 82	5.52
Cu : bip : Tartaric acid	−0.0970	1 672	14925	− 640	1.84	6.27
Cu : bip : Citric acid	−0 0920	1.795	14600	− 315	1.74	5.56
Cu : bip : Succinic acid	−0 0920	1.748	14184	+ 101	1 52	5.55
Cu : bip : Benzoic acid	−0.1100	1 403	14700	− 600	3.23	7.12
Cu : bip : Phthalic acid	−0.1000	1.516	14390	− 105	2 14	6.72
Cu : bip : Salicylic acid	−0 0880	1.646	14490	− 205	1 52	5.70
Cu : bip : Mandelic acid	−0 0900	1 566	14600	−:315	1.82	5.71
Cu : bip : Gallic acid	−0.0530 } −0 2800 }	1 118 } 2.630×10^{-1} }	14285	0	2 32	5.82
Cu : bip : Glycine	−0.1070	1.416	15640	−1355	6.8	9.79
Cu : bip : Valine	−0.1490	1.010	15837	−1505	7.8	9.88
Cu : bip : Serine	−0.1150	1.453	15790	−1552	8.5	10.23
Cu : bip : Leucine	−0.0105 } −0.3150 }	1.182 } 4.786×10^{-2} }	15267	− 982	6.65	8.62
Cu : bip : Resorcinol	−0.0975	1.995	14285	0	2.10	5.73
Cu : bip : Catechol	−0.0880 } −0.3880 }	1.058 } 2.270×10^{-1} }	14184	+ 101	—	—

TABLE 2—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : BIPYRIDYL WITH SECONDARY LIGANDS 1:2:1

Complex	$E_{\frac{1}{2}}$ V vs. SCE	Formal Rate Constant "K_f" 1×10^{-4} cm sec^{-1}	ν_{max} cm^{-1}	$\Delta\nu$ cm^{-1}	Activation energies Q_D Kcal	Q_e Kcal
Cu : Bipyridyl	−0.2000	0.5679	13927	0	7.83	10.21
Cu : bip : Formic acid	−0.1420	1 5030	13927	0	7.00	9.21
Cu : bip : Oxalic acid	−0.2000	1.0920	15625	−1698	6 80	8 00
Cu : bip : Tartaric acid	−0.1730	1.0310	13927	0	7.32	10.12
Cu : bip : Citric acid	−0.1600	1.1530	13927	0	6 56	7.87
Cu : bip : Succinic acid	−0.1620	1.3850	13927	0	6 12	7.77
Cu : bip : Benzoic acid	−0.2000	0.7162	13700	+ 227	9.52	11.23
Cu : bip : Phthalic acid	−0.1600	1.3730	13800	+ 127	9 20	10.71
Cu : bip : Salicylic acid	−0.1360	1.5730	13700	+ 227	8.72	10.21
Cu : bip : Mandelic acid	−0 1440	4.5900	13940	− 13	8 51	9.23
Cu : bip : Gallic acid	−0.2120	1.0350	13800	+ 127	6 23	9.02
Cu : bip : Glycine	−0 2570	1.1140	13927	0	9 20	12.28
Cu : bip : Valine	−0 2650	1.2620	13927	0	9.70	12.56
Cu : bip : Serine	−0.2600	1.1680	13927	0	9 80	13.26
Cu : bip : Leucine	−0.2420	1.1690	13927	0	8.50	11.26
Cu : bip : Resorcinol	−0 1840	1.5320	13927	0	6 92	10.30
Cu : bip : Catechol	−0 1100 −0 4050	0.9298 0.3710	13927	0	7 82	10 87

TABLE 3—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : PHENANTHROLINE WITH SECONDARY LIGANDS 1.1·1

Complex	$E_{\frac{1}{2}}$ V vs SCE	Formal Rate Constant "K_f" 1×10^{-4} cm sec^{-1}	ν_{max} cm^{-1}	$\Delta\nu$ cm^{-1}	Activation energies Q_D Kcal	Q_e Kcal
Cu : Phenanthroline	+0.0120 −0.3100	0.7925 0.4298	13927	0	4 20	7.65
Cu : phen : Formic acid	+0 0020 −0 1960	1.0640 1.9630	14490	− 563	3.72	7 23
Cu : phen : Oxalic acid	+0.0100 −0.1670	1.1550 1 2910	15625	−1698	5 32	9.12
Cu : phen : Tartaric acid	−0.0050 −0.1918	0.9183 1.3740	15433	−1506	4.60	8 83
Cu : phen . Citric acid	−0.0015 −0 2085	1 2290 1.0730	14925	− 998	4 12	8 78
Cu : phen : Succinic acid	0.0000 −0.1960	0 9629 1 2210	15151	−1224	3.29	8 12
Cu : phen : Benzoic acid	+0.0105 −0.1800	1.0750 1 9630	15625	−1698	5 05	9.25
Cu : phen : Phthalic acid	−0.0100 −0.1930	1 1790 1 6900	14285	− 358	5 24	9.92
Cu : phen . Salicylic acid	0 0000 −0.1930	1 2170 1 2170	14285	− 358	5 13	10.56
Cu : phen · Mandelic acid	−0.0050 −0.2050	1 1030 2 1020	14285	− 358	5 31	10.23
Cu : phen : Gallic acid	−0.0900 −0.3400	1.7020 0 2520	13927	0	6 23	10 56
Cu : phen : Glycine	−0.0015 −0.2050	3 8230 0 7982	16130	−2203	9.20	11 50
Cu : phen : Valine	−0.0080 −0 1900	2 3790 0 4410	16390	−2463	9.85	12.67
Cu : phen : Serine	−0.0045 −0.2090	3.6040 4.1820	16390	−2463	9 56	11.82
Cu : phen : Leucine	−0.0020 −0.2100	2.8790 0.4808	16130	−2203	9 12	12.32
Cu : phen : Resorcinol	+0.0035 −0 1680	1.3320 1.2210	15870	−1943	7.12	13.21
Cu : phen : Catechol	+0 0090 −0.1850	1.3030 1.0250	16130	−2203	7.84	14.04

TABLE 4—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : PHENANTHROLINE WITH SECONDARY LIGANDS 1.2.1

Complex	$E_{\frac{1}{2}}$ V vs SCE	Formal Rate Constant "K_f" 1×10^{-4} cm sec^{-1}	ν_{max} cm^{-1}	$\Delta\nu$ cm^{-1}	Activation energies Q_D Kcal	Activation energies Q_s Kcal
Cu ; Phenanthroline	+0.0180 −0.3080	2.1510 0.0755	13927	0	6.80	10.90
Cu · phen · Formic acid	+0.0065 −0.3650	1 8320 0.3850	13927	0	5.72	9.99
Cu · phen Oxalic acid	+0 0015 −0.3750	1 9370 0.2061	15151	−1224	6.21	10.97
Cu · phen · Tartaric acid	+0 0045 −0 4200	1.9369 0.3109	13927	0	5.94	10.67
Cu · phen : Citric acid	+0 0050 −0·4360	1.9560 0.3543	13927	0	5.50	9.23
Cu · phen : Succinic acid	0.0000 −0·4300	1.9560 0 2291	13927	0	5 50	9.45
Cu · phen · Benzoic acid	−0 0030 −0.3600	1.7970 0.2368	13927	0	6.23	9 72
Cu · phen Phthalic acid	−0.0060 −0.4680	1 9110 0.4133	13927	0	7 88	10.84
Cu : phen : Salicylic acid	−0 0020 −0 3600	1 9350 0.4360	13927	0	7 77	10 74
Cu · phen Mandelic acid	−0.0120 −0 4650	1 7860 0.3038	13927	0	7.99	10 47
Cu : phen Gallic acid	−0.0560 −0.4905	2.5840 0 1141	13927	0	8 47	11.23
Cu · phen Glycine	−0 0040 −0 4500	1 8660 0 4560	13927	0	11.04	18.60
Cu phen Valine	−0.0015 −0 3880	3.4100 0.8511	13927	0	11 47	19.56
Cu : phen Serine	+0 0030 −0.3915	2 6000 0.6621	13927	0	10 25	18.23
Cu · phen · Leucine	−0 0030 −0.3630	3.0140 0.1035	14660	− 733	11 23	17.14
Cu : phen · Resorcinol	−0 0010 −0 3900	1.9190 0 1480	13927	0	8 20	16.21
Cu · phen · Catechol	−0 0040 −0.4500	2.3090 0.2528	13927	0	9 20	18.40

TABLE 5—SPECTRAL DATA OF MIXED LIGAND COMPLEXES OF Cu(II) WITH BIPYRIDYL IN ULTRAVIOLET REGION

Secondary ligands	Complex	1 1.1 λ_{max}(nm) 1st Peak	1 1.1 λ_{max}(nm) 2nd Peak	1:2.1 λ_{max}(nm) 1st Peak	1:2.1 λ_{max}(nm) 2nd Peak
	Bipyridyl	176	228	276	228
	Cu · bip	296,306	216	294,306	218
	Cu : bip . Formic acid	294,304	234 (sh)	290,—	228
Aliphatic acids	Cu bip · Oxalic acid	294,304	244	292,—	—
	Cu · bip . Tartaric acid	294,304	240 (sh)	292,304 (sh)	230
	Cu . bip · Citric acid	294,304	238	280,304 (sh)	228
	Cu bip · Succinic acid	294,304	—	294,304	236 (sh)
	Cu · bip . Benzoic acid	294,304	218 (sh)	293,304	—
	Cu · bip . Phthalic acid	294,304	200	293,304	230 (sh)
Aromatic acids	Cu bip Salicylic acid	294,304	200	293,304 (sh)	236 (sh)
	Cu · bip Mandelic acid	294,304	200	293,304	236 (sh)
	Cu bip · Gallic acid	294,304	200	— —	220
	Cu bip · Glycine	294,304	234	294,304	—
Amino acids	Cu · bip . Valine	294,304	236	294,304	—
	Cu : bip : Serine	294,304	233	294,304	—
	Cu . bip : Leucine	294,304	234	294,304	—
Phenols	Cu : bip : Resorcinol	294,304	210	268 —	—
	Cu : bip : Catechol	294,304	214	276 —	—

TABLE 6—SPECTRAL DATA OF MIXED LIGAND COMPLEXES OF Cu(II) WITH PHENANTHROLINE IN ULTRA-VIOLET REGION

Secondary ligands	Complex	λ_{max}(nm) 1:1 1st Peak	λ_{max}(nm) 1:1 2nd Peak	λ_{max}(nm) 1:2.1 1st Peak	λ_{max}(nm) 1:2.1 2nd Peak
	Phenanthroline	258	220,—	—	— — —
	Cu : phen	268	218,198	264	219,197,—
	Cu : phen : Formic acid	266	218 —	266	218,197,—
	Cu : phen : Oxalic acid	266	218,184	265	218,198,—
Aliphatic acids	Cu : phen : Tartaric acid	266	218,196	264	218(sh),182
	Cu : phen : Citric acid	266	210,183	265	218,194,183
	Cu : phen : Succinic acid	266	210,196,184	265	218,194,183
	Cu : phen : Benzoic acid	266	218,188	263	218,190
	Cu : phen · Phthalic acid	266	218,190	263	218,—
Aromatic acids	Cu · phen : Salicylic acid	266	218,198	263	218,—
	Cu : phen · Mandelic acid	266	218,196,184	262	218,194,184
	Cu : phen · Gallic acid	266	218,200	261	218,194
	Cu · phen : Glycine	266	216,198,—	265	218,197
Amino acids	Cu : phen : Valine	266	218,198,183	266	218,197
	Cu . phen · Serine	266	218,196,182	265	218,197
	Cu : phen : Leucine	266	218,198,—	265	218,197
Phenols	Cu : phen · Resorcinol	266	— ,190	266	216(sh),190
	Cu : phen · Catechol	266	— 192	266	218(sh),—

Discussion

In the simple ligand field description of metal ion complexes, one is concerned with the effect of ligands on the energies of the d levels of metal ions. Since octahedral, square-planar and tetrahedral fields cause different splitting of the five d orbitals, geometry will have a pronounced effect upon the d-d transitions in a metal ion complex and spectral data for these transitions should provide information about the structure of complexes.

Copper complexes have a distorted octahedral structure in aqueous solution[16], with four short-ligand bonds in one plane (XY) and two longer metal-ligand bonds lying along the Z axis above and below the plane. Such complexes give rise to one absorption band[17] in the visible region near 16000 cm^{-1}. The relative order of these transitions will depend upon the extent of axial metal-ligand interaction.

In a six-coordinated complex of Cu(II) (distortion along Z direction) the nine d electrons are accommodated in different orbitals as follows :

$$(d_{xy})^2(d_{yz})^2(d_{xz})^2(\sigma^*_{z^2})^2\sigma^*_{x^2-y^2})^1$$

Postulating that the complex is oriented[18] at the electrode surface such that the square plane (XY-plane) is perpendicular to the electrode surface, the $(\sigma^*_{x^2-y^2})$ orbital as also the d_{xy} orbital point toward the electrode. The two electrons, needed for electro-reduction and coming from the electrode, shall be accommodated in the lowest lying vacant orbitals. The $\sigma^*_{x^2-y^2}$ is incapable of receiving the incoming electrons due to its low electron affinity. Out of the two suitably oriented orbitals, namely d_{xy} and $\sigma^*_{x^2-y^2}$, the former is low lying and this must be vacated prior to the electron transfer. Under strong influence of the electrode field, two electrons are promoted to the next higher vacant orbitals. This promotion energy required for the process will naturally depend upon the energy difference between the non-bonding T_{2g} orbitals and the antibonding E_g^* and A_{1g}^* orbitals and hence the ease of the reduction of the depolarizer may be correlated with the ligand field strength.

$E_{1/2}$ and ν_{max} : For the sake of correlation of the redox properties of these complexes with their spectral behaviour, the polarographic characteristics

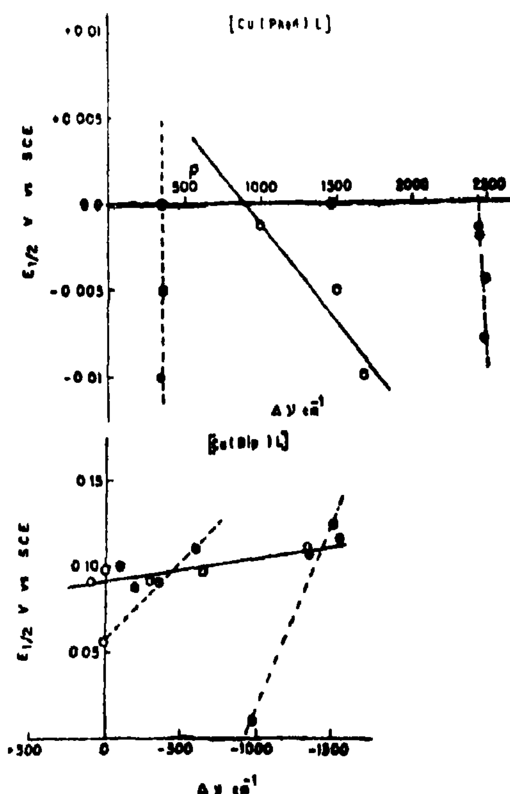


Fig. 1 Plot of $E_{1/2}$ vs spectral shift of absorption band for Cu(II) complexes of the type [Cu(bip)L] and [Cu(phen)L], L=—aliphatic acids, - - - - - aromatic acids, -·-·-·- amino acids.

($E_{1/2}$ and K_f) have been tabulated along with the ligand field band of the complexes concerned in Tables 1-4. It will be seen that in the ternary complexes involving aliphatic acids, aromatic acids and phenols with the exception of those involving oxalic and benzoic acid, the half-wave potential shifts towards comparatively more positive values and the rate constant increases. This means that the ease of reduction increases. In case of ternary complexes involving amino acids, the $E_{1/2}$ shifts towards more negative values while the value of rate constant decreases or the rate of electron transfer decreases. A further observation is that the ease of reduction as evidenced by $E_{1/2}$ values also decreases with increasing ligand field-strength A plot of half-wave potentials against the difference of the energy of the ternary complex and the parent binary complex gives a straight line (Fig 1) for this series of complexes lending support to the above statement. Vlček[1] made similar observations in case of $Fe(phen)_2X_2$, $Fe(phen)_2X_2$ series, NiL_3^-, NiL_3^{2-} series and for cobalt and chromium complexes.

Reduction is regarded as comprising the acceptance of an electron into the lowest unoccupied, or singly occupied orbital of the depolarizer[19,20]. For reduction process, the rate and mechanism of the overall process will be dictated by the localization and energy of the lowest orbital. If the orbital in question has a high electron affinity, it may be possible for depolarizer particle to react directly with the electrode with only slight changes in configuration. A rearrangement will be necessary if the orbital has a low electron affinity since direct reduction in this instance will require a very large negative applied potential The complexes of these series of the type [Cu(bip)L] and [Cu(phen)L] have confirmed essential correctness of the foregoing arguments In such complexes, the lowest unoccupied orbital is an antibonding e_g^* orbital of very low electron affinity (much lower than that of the T_{2g} orbitals) so that direct reaction with the electrode is impossible A configuration change, to give a structure capable of direct reaction with the electrode, must therefore take place whose energy may be regarded as a function of the difference between the ground and excited states i e the energy of the transition state depends on the ligand field strength of the complex.

A perusal of data on Cu(II) phenanthroline series (Tables 3 and 4) of mixed ligand complexes shows that it does not confirm fully to the conclusion arrived at for the corresponding bipyridyl series of mixed-ligand complexes of Cu(II). In fact, the ease of reduction seems to be a composite of several structure and non-structural factors[21]. At least one factor which may cause this difference in behavioural pattern is prominently the delicate balance between two opposing forces of σ and π donation character of the ligands The back bonding may reduce the electron density on the metal ion and thus facilitate the electron transfer and hence easier reduction of the depolarizer. The π-bond character of phenanthroline is much greater compared to that of the bipyridyl as a ligand and hence flow of electron density from the filled metal orbitals into the π^* antibonding orbitals of the aromatic ring system of phenanthroline is much more facile.

Q_D and ν_{max} : An important condition governing all electrode processes follows from the Frank-Condon principle which states that electron transfer process takes place much more rapidly than configurational changes. Electron transfer may thus be regarded as occuring adiabatically and with negligible activation energy[22]. It follows that the electronic states of the reactants (electrode and depolarizer) must be equal before electron transfer takes place, i e. the energy necessary to abstract one electron from its initial position must be exactly supplied by the energy with which it is bound in its final position in the depolarizer. If this occurs, the electronic energy of the depolarizer is changed prior to reduction and the formation of the transition state requires considerable energy (rearrangement activation energy) which forms a large part of the total activation energy for the process as a whole. Estimated values of Q_D give a straight line relationship with $\Delta\nu$ (Fig 2) supporting the above statement Vlček made similar observations with following series of complexes: $Co(NH_3)_5X^{n+}$, $Co(CN)_5X^{n-}$, $CoOX_n(am)_m^n$ $Rh(NH_3)_5X^{n+}$, $Co(NH_3)_4X_2^{n+}$, $Cr(NH_3)_5X^{n+}$, $CrOX_n(am)_m^n$ and $Rh(en_2)X_2^{n+}$.

UV spectra : In the uv region two transitions are observed for primary ligands alone indicating $\pi\pi^*$ and $n\pi^*$ transitions according to Robert D. McAlpine[23] In the present conditions, bipyridyl absorbs at 228 nm and 276 nm indicating the transition $\pi\pi^*$ and $n\pi^*$, respectively. The $n\pi^*$ transition seems to be stronger than the $\pi\pi^*$ transition. A similar spectra have been obtained in the case of phenanthroline molecule i e. phenanthroline molecule absorbs at 220 nm and 258 nm indicating the $\pi\pi^*$ and $n\pi^*$ transitions, respectively. But in this case the $\pi\pi^*$ transition seems to be stronger than the $n\pi^*$ transition.

In the spectra of binary complexes, [Cu(bip)] 1 : 1 and 1 : 2, there is a bathochromic shift in $n\pi^*$ transition and also splitting (296 nm and 306 nm) is observed on complexation due to the possibility of metal-ligand interaction. Back donation from metal filled-orbitals to vacant low-lying anti-bonding π^* orbitals of bipyridyl cause hypsochromic shift in $\pi\pi^*$ (218 nm) transition. But in the binary complex, $\pi\pi^*$ transition seems to be stronger than $n\pi^*$ transition. In case of phenanthroline complexes, on complexation with metal ion bathochromic shift in $\pi\pi^*$ (267 nm) and hypsochromic shift and splitting in $\pi\pi^*$ (218 nm, 197 nm) are observed. In the case of 1 : 1 complex, $\pi\pi^*$ transition is not split properly but a shoulder is observed at 218 nm. In the 1 : 2 complex, split band at 218 nm is stronger than the band at 197 nm.

A very small bathochromic shift is observed in $n\pi^*$ transition on addition of secondary ligands

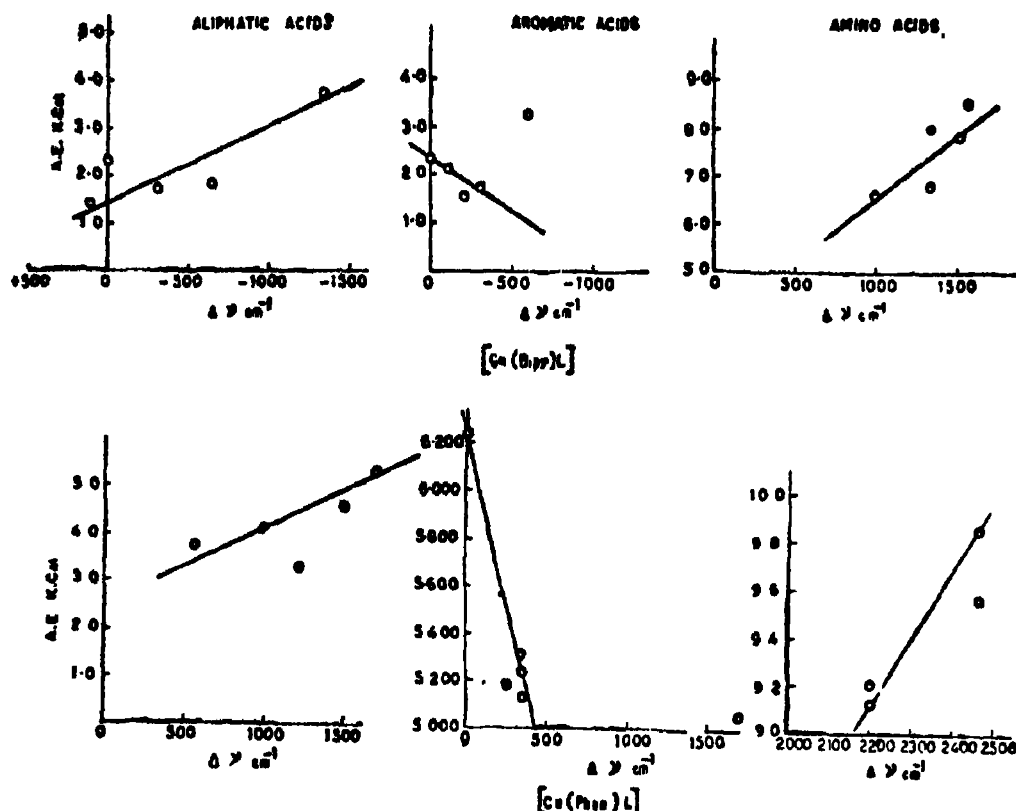


Fig 2. Dependence of activation energy of the electrode process upon the absorption band shift of complexes [Cu(bip)L] and [Cu(phen)L]

in 1 : 1 : 1 mixed ligand complexes. In aliphatic series, peak of $\pi\pi^*$ is obtained only in the case of [Cu(bip)Ox] and [Cu(bip)Cit] complexes A shoulder is obtained in [Cu(bip)Tar] complexes and no $\pi\pi^*$ band is observed in the case of [Cu(bip)Suc] complex In amino acid series, shoulder of $\pi\pi^*$ band is observed Further observation shows that the presence of secondary ligands possessing a ring e.g. phenols cause further hypsochromic shift in $n\pi^*$ band. A shoulder is obtained in the case of [Cu(bip)Ben] complex. But in other complexes of aromatic acid series, a hypsochromic shift in $\pi\pi^*$ band (200 nm) is observed perhaps, due to the possibility of ligand-ligand interaction. But in the case of aliphatic acids and amino acids, there is no possibility of $\pi\pi^*$ interaction due to the absence of ring. In the case of 1 : 2 : 1 ternary complexes of [Cu(bip)L] the splitting of $n\pi^*$ band (296 nm and 306 nm) is observed in each complex but there is no $\pi\pi^*$ band except in the case of [Cu(bip)Tar], [Cu-(bip)Cit] and [Cu(bip)Gal]. In the case of phenanthroline mixed-ligand complexes 1 : 1 : 1 and 1 . 2 : 1, the presence of secondary ligands (possessing ring) causes further hypsochromic shift in $\pi\pi^*$ indicating ligand-ligand interaction, while in the case of aliphatic and amino acids there is no further split showing their inability for ligand-ligand interaction. Possibility of metal-metal interaction is not indicated.

On comparing the data on the complexes of bipyridyl and phenanthroline with Cu(II), opposite results are observed In bipyridyl, splitting is obtained in $n\pi^*$ while in the case of phenanthroline $\pi\pi^*$ splitting is observed. This behaviour can be explained on the basis of the structure of these ligands The nature of phenanthroline can be attributed to the hindered rotation along the fused axis while in the case of bipyridyl, due to the free rotation along joining axis, the splitting of $n\pi^*$ transition is observed. In the case of the mixed-ligand complexes of phenanthroline, the effect of secondary ligand is appreciable indicating that the phenanthroline is a better ligand than bipyridyl which is also confirmed by the polarographic studies of these complexes.

The results obtained on comparing the spectral characteristics with the polarographic behaviour are not very revealing. Plots of $E_{\frac{1}{2}}$ vs ν are given in Fig 3. A linear relationship is obtained only for the complexes [Cu(bip) aliphatic acids], [Cu(bip)-aromatic acids] and [Cu(phen) aromatic acids]. This relationship is not very surprising A linear relationship between $E_{\frac{1}{2}}$ and ν shall be obtained only when the complexes in the series fulfil a number of important conditions like (i) the interatomic distances in the reduced and oxidised forms do not differ much, (ii) the donor or acceptor part of the molecule remains almost the same throughout the series, (iii) the change of solvation energy accompanying the redox transition and the change of

[Cu · Bip] 1 : 1 With aliphatic acids (A) and aromatic acids (B)

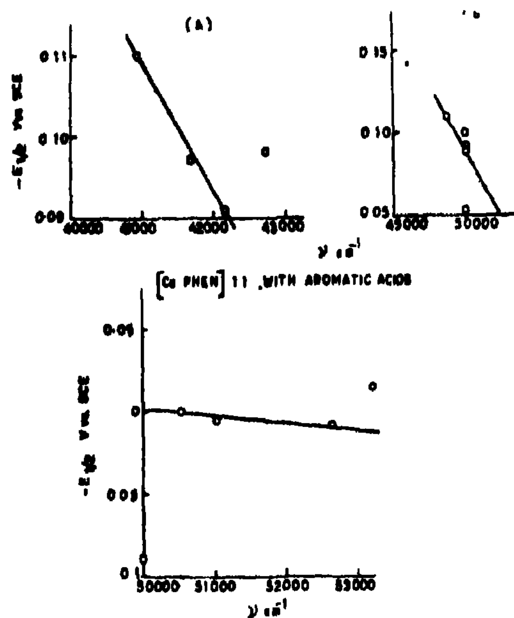


Fig. 3. Dependence of half wave potential on spectral studies (charge transfer spectra)

entropy for the redox couple remain constant throughout the series[2].

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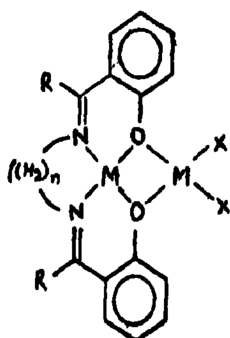
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Antiferromagnetic Interaction in Binuclear Copper(II) Complexes Involving Tetradentate Schiff Bases

P K. BHATTACHARYA

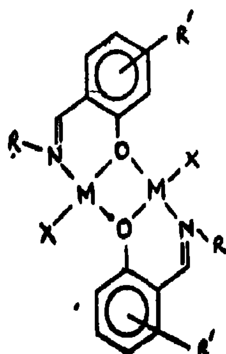
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THE area of homodinuclear complexes has invited the attention of many chemists because of their interesting electronic spectral and magnetic properties and their application as homogeneous catalysts in molecular activation processes and as models for the metalloenzymes and the developments have been comprehensively reviewed[1-3] Sinn and Harris have reported the binuclear and trinuclear complexes of the type [Cu(TSB) Cu Cl_2] and [$Cu(TSB)_2$. Cu]$(ClO_4)_2$, where TSB is various tetradentate Schiff bases derived from salicylaldehyde and 2-OH-acetophenone The mononuclear complex of the tetradentate Schiff base has an additional lone pair of electrons over the two phenolate O^-. It can react with the chlorides of the same metal when a homobinuclear complex results However, if the TSB complex of a metal ion is made to react with the chloride of another metal ion, a heterobinuclear complex results.



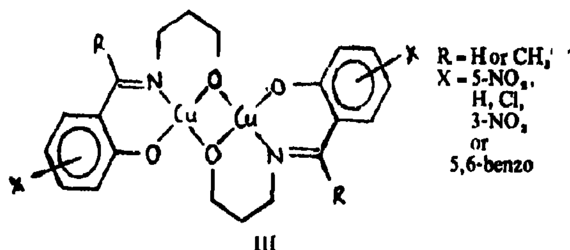
R = H or CH_3
n = 2, 3, 4, or 6
X = Cl^-, Br^- or NO_3^-
M = Cu(II) or Ni(II)

I



R = CH_3, C_2H_5 or C_4H_9
R′ = H or 5-Cl
X = Cl or Br
M = Cu(II)

II

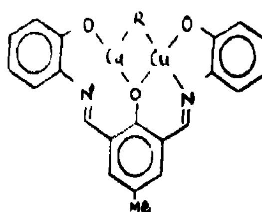


III

Synthesise of binuclear Cu(II) complexes of the type II[4] and III[5,6] have also been reported, where the phenolate O^- of bi- or tri-dentate Schiff base acts as bridge between the two Cu(II) centres.

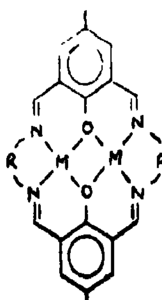
Binuclear complexes of Cu(II) was also obtained by the treatment of cupric isobutyrate with the Schiff bases derived from the reaction of *o*-aminophenol or alkanolamine with 3-formyl-5-methylsalicylaldehyde (IV)[7]. This differs from the earlier complexes in the fact that both the metal ions are bound to the same ligand. The ligand provides two coordination sites for the metal ions to be bound.

Formation of closed double compartment Cu(II) binuclear complexes, bridged through O^-, have also been reported in the cases of macrocyclic Schiff base ligands obtained by condensing 2-OH isophthalaldehyde with diamines (V)[8,9].



R = OMe

IV



R = $(CH_2)_2$– or –$(CH_2)_3$–
M = Cu(II), Ni(II), Co(II), Fe(II) or Mn(II)

V

In these binuclear Cu(II) complexes it has been observed that the magnetic moments are subnormal and decrease with decreasing temperature. This has been explained to be due to antiferromagnetic interaction between the two Cu(II) centres. In dimeric Cu(II) acetate, it was pointed out by Martin and Figgis[10] and later by Kettle[11] that the distance between the two Cu(II) centres is less and hence a weak metal interaction is possible. However, in the complexes of the present type, Cu(II)-Cu(II) the distance is large and hence it seems unlikely that the direct exchange due to overlap of copper d orbitals is significant. The possible exchange pathway is super exchange involving copper $d_{x^2-y^2}$ and oxygen P_x orbitals. This interaction gives rise to a diamagnetic ground state and an excited paramagnetic triplet state. The separation between the two states is equal to 2J value, where J is the value of spin exchange interaction. It is given by the following equation :

$$J=\int\int(\Psi_{a(1)}\Psi_{b(2)})/Hex/\Psi_{b(1)}\Psi_{a(1)}\partial T_1\,\partial T_2$$

where the hamiltonian operator,

$$Hex=\frac{e^2}{r_{12}}+\frac{2a^*2b^*e^2}{R}-\frac{2b^*e^2}{r_{1b}}-\frac{2a^*e^2}{r_{2b}}$$

If $2J \gtrless KT$, all the molecules are in the singlet ground state and the binuclear complex is diamagnetic. When $2J = KT$, the magnetic susceptibility depends on the Boltzman population of the states. The temperature dependance of the susceptibility (χ_m) is given by the equation suggested by Bleany and Bowers.

The magnitude of J can be determined from a fit of the experimental data of χ_m and T to the above equation or may be estimated from T_{max} (the temperature at which χ_m is maximum) in the plot of T against magnetic susceptibility.

For the exchange interaction to occur between the two Cu(II), it is necessary that the binuclear complex should have a planar structure. Any distortion from planarity would reduce the overlap of Cu(II) $d_{x^2-y^2}$ orbitals with oxygen p_x orbital, and the exchange interaction is weakened. A convenient measure of the degree of distortion from planarity is the angle T between the plane of the Cu_2O bridge and that of the remaining ligands. For a complete planar structure it will be zero and will increase with tetrahedral distortion at the two Cu(II) centres. On this basis, super exchange in the complexes of the type II should be more than that in I[8]. It is actually observed that type II complexes exhibit much larger singlet-triplet separation (300 cm^{-1} or more) and the magnetic property do not differ significantly from complex to complex. In complexes of type I, the J value is less and the magnetic property differs significantly from compound to compound. These properties can be explained by considering that complexes II have *trans* structure. The *trans* structure helps the complex to attain more of planar structure and hence the exchange interaction is more. If R groups on N are bulkier, there is steric distortion towards tetrahedral and magnetic moment goes up. The band position in the ligand field spectra of these complexes also show that the Cu(II) in these binuclear complexes is in a square planar field. With substitution of bulky R groups, there is tetrahedral distortion with λ_{max} moving to higher wavelength region. Thus, there is a linear relationship between the d-d band wavelength and the magnetic moments of the complexes. The same relationship holds good in type III complexes also[8,12].

In the complexes of type I, the two phenolate O^- of the TSB are on the same side. In [Cu(TSB)] itself, the structure of the ligand around Cu(II) is distorted from planarity. In the binuclear complexes, on coordination with $CuCl_2$, the O,O>Cu<Cl,Cl part has a pseudo tetrahedral structure. This induces more planarity on the [Cu(TSB)] part. It was observed by Sinn[4] that if one of the metal ions is in a planar environment, the adjacent metal ion will be distorted away from planarity, and if one of them is in a tetrahedral environment, the adjacent metal will be distorted away from tetrahedral geometry. As distortion from planarity increases, there is a lowering in the antiferromagnetic interaction, resulting in increase in the magnetic moment. But with tetrahedral distortion there is a lowering in the ligand field with consequent increase in λ_{max}. Thus, linear relationship between magnetic moment and λ_{max} value holds good in these complexes also.

In case of type I [Cu(TSB)$CuCl_2$] complexes, it was observed[1] that there is a steady increase in the magnetic moment and λ_{max} values as we move to the TSB with increasing length of the carbon chain joining the N atoms This is because there is an increased distortion from planar to pseudo tetrahedral form in the geometry of the [Cu(TSB)] with increasing chain length. Increasing distortion from planar towards tetrahedral geometry causes an increase in the magnetic moment and a shift to lower energy of the ligand band.

There is no systematic relation observed between the magnetic moments and Cu-O-Cu′ angle in type II and III complexes. This is probably because the angle does not vary enough to show a significant effect. Since the super exchange takes place between the Cu(II) centres and O^-, the environment around them have the maximum effect on the J value[12].

In these complexes, (I, II and III), substitution over the phenyl ring of the Schiff base can affect the J value to the extent they alter the Cu-O-Cu bridge via alteration of molecular packing. Nature of R over >C=N part also does not affect the properties significantly. TSB derived from 2-OH-acetophenone or 2-OH-benzophenone forms binuclear Cu(II) complexes with magnetic moment not significantly different from TSB derived from salicylaldehyde[18].

In case of type I binuclear complexes of TSB of N,N′-ethylene *bis*salicylaldimine (ES) and X=Cl,

it was observed that there is a possibility of linkage of the halogen with the Cu(II) of the adjacent molecule making it five coordinated and weakening one of the Cu-O bonds This results in a weakening of the antiferromagnetic interaction and lowering of J value.

Sinn and coworkers[14] studied the pressure dependence of magnetic susceptibility in the range 1−3000 atm. In cases of type II complexes there is little effect on magnetism with X=Cl or Br. This is because they have very similar structure, and the electronic effect, which might have been affected, is not evident.

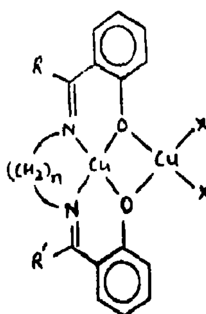
However, when $X=NO_3^-$[15], the second oxygen of the already coordinated NO_3^- is in close proximity to the Cu(II) of another binuclear complex Thus, there is formation of a weaker Cu-O bond due to intermolecular interaction and the geometry at each Cu(II) is square pyramidal. This apical bond reduces the super-exchange overlap, reducing J value. The way it is brought about is not clear because the Cu-O-Cu bridge angle is not affected significantly.

The spectral characteristics of the binuclear complexes are also interesting. In case of type III complexes of bidentate Schiff bases[4], only one band is observed, though shifted from the band position of the mononuclear complex This shows that the two Cu(II) atoms have equivalent ligand field in type II complex The position of the band also shows that the structure of the two centres is planar and this is in keeping with the *trans* structure The same is true in case of type III complexes also However, in type I complexes involving TSB, there are two non-equivalent Cu(II) centres and hence two bands are observed. In the $CuCl_2$ part bonded to the two O^- of the Cu(TSB), Cu(II) is in a tetrahedral environment and hence band is observed *in the region 8000-12000* cm^{-1} as expected in tetrahedral Cu(II) complexes. The original band of mononuclear TSB complex, occuring at ~17000 cm^{-1}, shows a shift on coordination with $CuCl_2$. The band shifts to the higher energy region indicating that the complex ligand becomes more planar when it coordinates with $CuCl_2$. This energy shift comfirms that there is formation of binuclear complex.

Their spectral studies also support the formation of the binuclear complex[4] There is an increase in the constraint on the vibration of the Schiff base part of [Cu(TSB)] on its coordination with CuX_2. This results in a shift of the ir bands of [Cu(TSB)] part in the region 1620, 1480, 1140, 1040 and 760 cm^{-1} to higher energy by about 5−10 cm^{-1} in the binuclear complex. The band near 1530 cm^{-1} is due to phenolic C-O stretching. This is most affected by the coordination of the [Cu(TSB)] to CuX_2 and shows a shift of about 15 to 20 cm^{-1}.

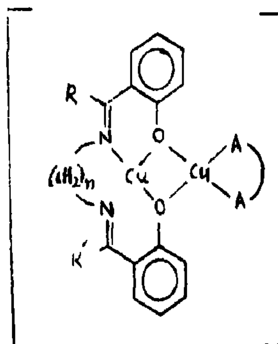
It is thus observed that the nature of X on the second copper centre may affect the properties of the [Cu(TSB)CuX$_2$] complexes. We have carried out[16] the study of binuclear Cu(II) complexes formed by the coordination of tetradentate Schiff base complex with a metal ion already bound to another bidentate ligand. Complexes of the type [Cu(TSB)Cu(A-A)]$(ClO_4)_2$ have been prepared where TSB=tetradentate Schiff bases like N-N'-ethylene (or propylene) *bis*salicylaldimine, N-N'-ethylene (or propylene) *bis*-2-OH-aceto-phenonimine, A-A=tertiary diamines like 2,2'-dipyridyl, 1,10-phenanthroline or 2-(2'-pyridyl) benzimidazole.

[Cu(TSB') CuX$_2$] and [Cu(TSB')Cu(A−A)]$(ClO_4)_2$ binuclear complexes have also been synthesized[17], where X=Cl or ClO_4, TSB' is an unsymmetrical tetradentate Schiff base like N-N'-ethylene (or propylene) salicylaldimine-2-OH-acetophenonimine or N-N'-propylene salicylaldimine-2 OH-1-naphthaldimine. [Cu(TSB)], where TSB= symmetrical or unsymmetrical tetradentate Schiff bases, were prepared by template synthesis followed by amine exchange[18,19]. [Cu(TSB)Cu(A-A)]$(ClO_4)_2$ complexes were synthesized by treating [Cu(TSB)] with [Cu(A-A)$(ClO_4)_2$]. The structure of the resulting binuclear complexes can be shown as below.



R = H
R' = H or CH_3
n = 2 or 3
X = Cl or ClO_4

VI



$(ClO_4)_2$
R = H or CH_3
R' = H or CH_3
n = 2 or 3
A-A = A¹, A² or A³

VII

The bridging phenolate O^- bond is very weak. Addition of water to the binuclear complexes breaks the bridge resulting in the separation of [Cu(TSB)] complex and $[Cu(H_2O)_6]Cl_2$, $[Cu(H_2O)_6](ClO_4)$ or [Cu(A-A)]$(ClO_4)_2$.

The complexes are not sufficiently soluble in organic solvents and hence molar conductance could not be determined. IR spectra show that in type VI complexes, ClO_4^- are in the outer sphere. IR band corresponding to ν_{C-O}, shifts to higher energy region

in the binuclear complex confirming the coordination of the phenolate O^- with the second Cu(II) centre. The shift in ν_{C-O} in the $[Cu(TSB)Cu(A-A)]^{2+}$ is of the same order as in $[Cu(TSB)CuX_2]$.

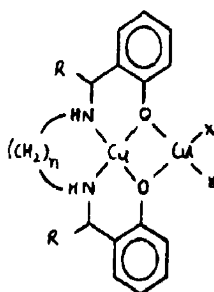
The reflectance spectra of the complexes show two d-d bands corresponding to the two non-equivalent Cu(II) centres. In type VI complexes, $>CuX_2$ centre shows a band at 8500-10000 cm^{-1} similar to that observed by Sinn and coworkers[1]. However, >Cu(A-A) part in type VII complexes shows a band at higher energy 12500 cm^{-1}. This is because A-A creates a stronger field than the two chlorides. The band, due to [Cu(TSB)] part in both types of binuclear complexes, show a shift from the free [Cu(TSB)] value This is because of the change in the planarity of [Cu(TSB)] on coordination with CuX_2 or $[Cu(A-A)]^{2+}$, as explained in earlier studies[8]. Further, coordination with $CuCl_2$ or $[Cu(A-A)]^{2+}$ also lowers the strength of Cu(II)-O bond in the [Cu(TSB)] part There is no significant difference in the lowering of [Cu(TSB)] band position in $[Cu(TSB) CuCl_2]$ or $[Cu(TSB)Cu(A-A)]^{2+}$.

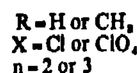
Magnetic moments of the complexes at room temperature were found to be lower than that expected for one unpaired electron on each Cu(II) ion. This indicates antiferromagnetic spin-exchange interaction. In these complexes also Cu-Cu distance is too big for direct interaction between the metal ion The super exchange must be taking place through σ interaction of Cu(II) $d_{x^2-y^2}$ orbitals with the s and p orbitals of the bridging diamagnetic O^- of the Schiff base Spin exchange integral J could not be calculated in the absence of variable temperature magnetic data and hence its value in type VI and type VII complexes could not be compared However, the lowering in the magnetic moment values in the two cases do not differ significantly

One interesting point of difference is that in case of type VI complexes, the lowering in the magnetic moment is less in complexes with TSB having a long $-(CH_2)_n-$ chain, as reported earlier[1]. But in the type VII complexes there is an increase in the lowering of magnetic moment in case of TSB with $-(CH_2)_3-$ than in case of TSB with $-(CH_2)_2-$. The explanation for this observation has to await X-ray crystal study of the complexes showing the extent of distortion in planarity at the two Cu(II) centres.

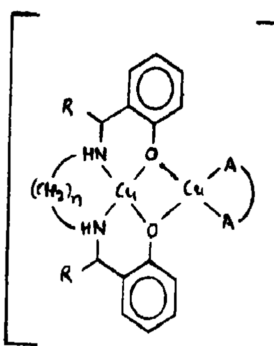
The possibility of super exchange interaction through the metal $d\pi$ orbital and the π orbitals of the O^- has been ruled out by the uv spectra of [Cu(TSB)], $[Cu(A-A)]^{2+}$ and the binuclear complex $[Cu(TSB)Cu(A-A)]^{2+}$. It is observed that the uv bands in the binuclear complexes have almost one to one correspondence with the bands of [Cu(TSB)] and $[Cu(A-A)]^{2+}$. Any interaction between the π orbitals of the TSB and bipyridyl through the metal ion should have changed the position of the near uv bands of the binuclear complex.

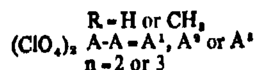
In order to prove this point, monomeric Cu(II) complexes of saturated tetradentate bases, obtained by the reaction of $NaBH_4$ on the Schiff base, were prepared. The extent of π delocalization i these complexes is lower than in the original [Cu(TSB)]. The mononuclear complex was treated with CuX_2 and $[Cu(A-A)(ClO_4)_2]$ to prepare complexes of the type $[Cu(MB)CuX_2]$ and $[Cu(MB)Cu(A-A)](ClO_4)_2$[20]. The structures are as follows.





VIII





IX

These complexes also show two d-d bands in the ligand field spectra corresponding to the two Cu(II) centres There is also a lowering in the magnetic moment showing super exchange interaction. The extent of lowering in the magnetic moment is of the same order as in case of type VI and type VII complexes This shows that restricting the π delocalization in the tetradentate ligand part does not affect the extent of super exchange. It can, therefore, be said that the π orbitals have no significant role to play in the super exchange interaction.

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Polarographic Reduction of In(III)

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Polarographic reduction of In(III) at different *p*H, temperature and concentration of sodium perchlorate has been investigated. A reversible and diffusion controlled wave is obtained at *p*H$\geqslant$3 having a half-wave potential of -0.512 volt vs SCE At lower *p*H values the magnitude of limiting current decreases and the wave becomes irreversible and kinetic-controlled. In the *p*H range of 0 4 to 0.8 a minimum in the limiting current region is visible when potassium chloride salt-bridge is used. In presence of small amounts of potassium hydrogen phthalate the reduction of In(III) becomes reversible even at low *p*H values.

MANY contradictory results exist in the literature on reduction of In(III) in various complexing and non-complexing supporting electrolytes[1-26]. Irreversible reduction of In(III) has been observed in halides, nitrate and perchlorate media[1-7]. On the other hand some workers have reported reversible reduction of In(III) in halides, thiocyanate and non-complexing media[8-15]. The reduction of In(III) has also been mentioned as quasi-reversible in certain supporting electrolytes[16-18].

The values of half-wave potentials of In(III) reported by various workers also show considerable discrepancy. Some investigators[19-22] were not even able to record the half-wave potentials due to the ill-defined nature of the wave, which was obtained by extrapolating the half wave potentials of In(III) in presence of varying concentrations of the ligand to zero ligand concentration.

The discrepancy observed by various workers in the nature of reduction and half-wave potential of In(III) prompted the authors to investigate the reduction of In(III) under different conditions. The polarographic reduction of In(III) has been systematically investigated at different *p*H, temperatures and concentrations of the supporting electrolyte ($NaClO_4$).

Experimental

Analytically pure grade reagents were used. Indium nitrate (Schuchardt, Munchen) was dissolved in dilute perchloric acid and was standardised against EDTA using PAN indicator[26]. Sodium perchlorate obtained from Koch Lab., England was used as the supporting electrolyte. Potassium chloride and potassium hydrogen phthalate used were BDH products.

Measurements of current and half-wave potentials were made with OH-105 Radelkis polarograph and a manual Toshniwal polarograph in conjunction with a PYE galvanometer (Cambridge, England). The temperature of all the solutions was maintained constant at 30±0.1°, except otherwise stated, by immersing the cell and saturated calomel electrode in an ultra thermostat. Measurements of *p*H were made on a NIG 333 digital *p*H meter. The *p*H of all the solutions was adjusted to the desired value by adding either dilute perchloric acid or CO_2-free sodium hydroxide solution.

The concentration of In(III) was kept at 2×10^{-4} *M*. The ionic strength was maintained constant at 0.1 by adding $NaClO_4$, except at lower *p*H values where perchloric acid was used to adjust the *p*H. The polarographic cell was connected to the reference electrode through a sodium nitrate or potassium chloride salt-bridge

Results and Discussion

Effect of pH: Polarograms were recorded at different *p*H values Two waves were obtained at low *p*H values in sodium perchlorate supporting electrolyte At *p*H>3 0 only one wave (first wave) was observed With lowering of *p*H the limiting current of the first wave decreased while a second irreversible wave appeared The half-wave potential of the second wave in presence of sodium nitrate salt bridge at *p*H values between 0.2 to 0.7 was -0.85 ± 0.02 volt vs SCE. Previous workers have also reported the existence of two waves of indium[4,10,20].

The values of current of the first wave at -0.6 volt vs SCE have been plotted against *p*H in Fig 1. The plot shows that when sodium nitrate was used as salt bridge the current remained almost steady upto *p*H 1 0 ($\approx$0.16 μA) and increased sharply at higher *p*H values. The maximum current (2.27 ± 0.03 μA) was observed at *p*H$\approx$3.0. The increase in current with increase of *p*H has been considered to be due to the formation of hydroxy complex $In(H_2O)_4(OH)_2$, which acts as a catalyst[10]. However, precipitation started at *p*H>3.4, which appeared to be complete at *p*H$\approx$4.5.

The waves obtained by recording polarograph at the same *p*H values are shown in Fig. 2. The wave become increasingly irreversible with decrease in *p*H of the solution. This observation was different from that of Lawson and Aikens[10] who reported

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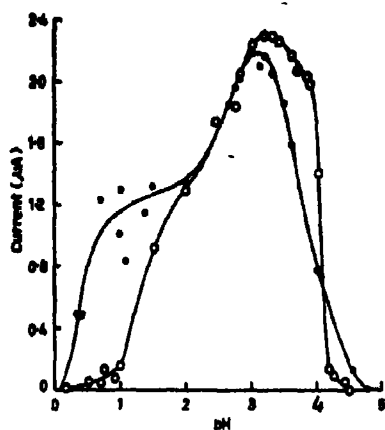


Fig. 1. Plot of current vs *p*H using sodium nitrate salt-bridge (○) and potassium chloride salt-bridge (●), for $2 \times 10^{-4}M$ In(III).

TABLE 1—EFFECT OF CONCENTRATION OF SUPPORTING ELECTROLYTE ($NaClO_4$) ON In(III) REDUCTION AT *p*H 3.1 AT 30°

In(III) = $2 \times 10^{-4}M$

Ionic strength (μ)	Diffusion current (μA)	$-E_{\frac{1}{2}}$ (Volt)
0.1	2 30	0.512
0.2	2 30	0.512
0.3	2 23	0.512
0.5	2.22	0.512
0.8	2.16	0.511

Effect of temperature : The half-wave potentials and limiting currents recorded at different temperatures at *p*H 3 are reported in Table 2. The temperature coefficient of limiting current was calculated by using the relation :

$$\text{Temperature coefficient} = \frac{2.303}{T} \log \frac{i_{T_2}}{i_{T_1}}$$

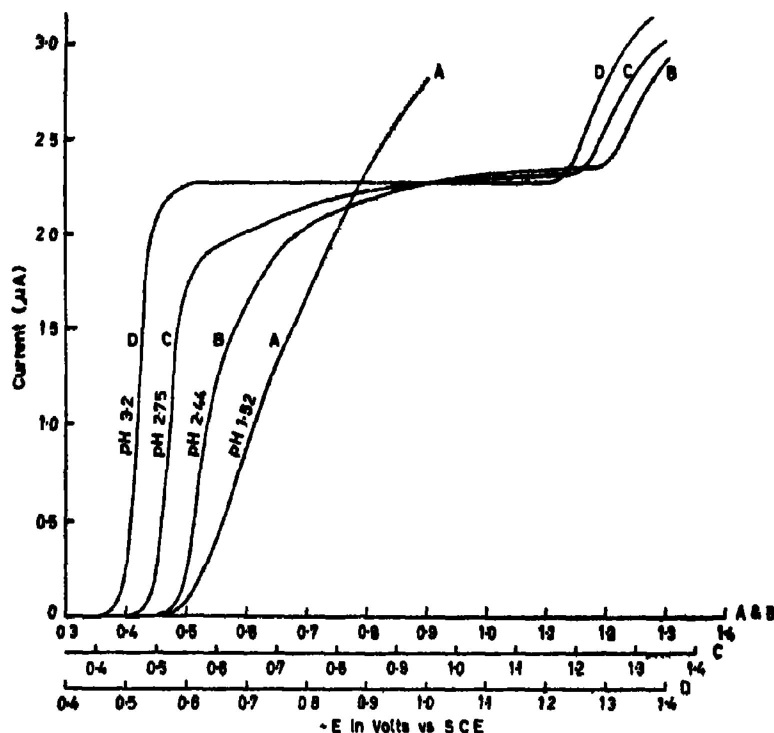


Fig. 2. Effect of *p*H on reduction of In(III) ($2 \times 10^{-4}M$) at 30° and μ = 0.1 ($NaClO_4$). Salt-bridge— sodium nitrate.

reversible waves at low *p*H values. The wave appeared reversible only at *p*H$\geqslant$3, wherein the plot of limiting current of In(III) vs its concentration or $\sqrt{h}$ (corrected height) gave a straight line passing through the origin. This indicated that the reduction at *p*H$\geqslant$3 was diffusion controlled. The reversible half-wave potential was found to be −0.512 V vs SCE.

Effect of concentration of supporting electrolyte : When the polarograms were taken at *p*H 3.1, it was noticed that the half-wave potentials remained nearly constant upto the ionic strength of 0.8 ($NaClO_4$) (Table 1). However, the diffusion current decreased slightly with increase in ionic strength.

TABLE 2—EFFECT OF TEMPERATURE ON In(III) REDUCTION AT *p*H 3.0

In(III) = $1.96 \times 10^{-4}M$ μ = 0.1 ($NaClO_4$)

Temp. °C	Limiting current (μA)	$-E_{\frac{1}{2}}$ (Volt)
15.0	1.78	0.530
25.0	2.10	0.518
30.0	2.20	0.512
37.5	2.30	0.502
49.0	2.73	0.495
54.0	2.91	0.488

The value of temperature coefficient from 15° to 54° has been found to be 0.0126, which comes to 1.26% per degree. The temperature coefficient value also suggested that the reduction wave was diffusion controlled. The temperature coefficient of the half-wave potential was ≈1.1 mV/degree.

Effect of KCl salt-bridge: Some investigators have reported abnormal behaviour of In (III) in presence of different concentrations of chloride ion[6, 7, 9, 15, 19, 23, 24]. It was therefore decided to study the specific influence of potassium chloride salt-bridge. Usually the observations were taken keeping the potassium chloride salt-bridge in solution for about 15 to 20 minutes. In some cases the polarograms were also recorded after placing the potassium chloride salt-bridge for longer periods.

The effect of potassium chloride salt-bridge is shown in Fig. 1. It can be observed that at low pH values the current was higher in presence of potassium chloride salt-bridge as compared to sodium nitrate salt-bridge. The current became nearly equal for both the salt-bridges at pH values between 2 and 3.

The current at low pH values did not remain constant when the readings were repeated at different intervals of time. Simultaneous readings have been taken at the same pH using sodium

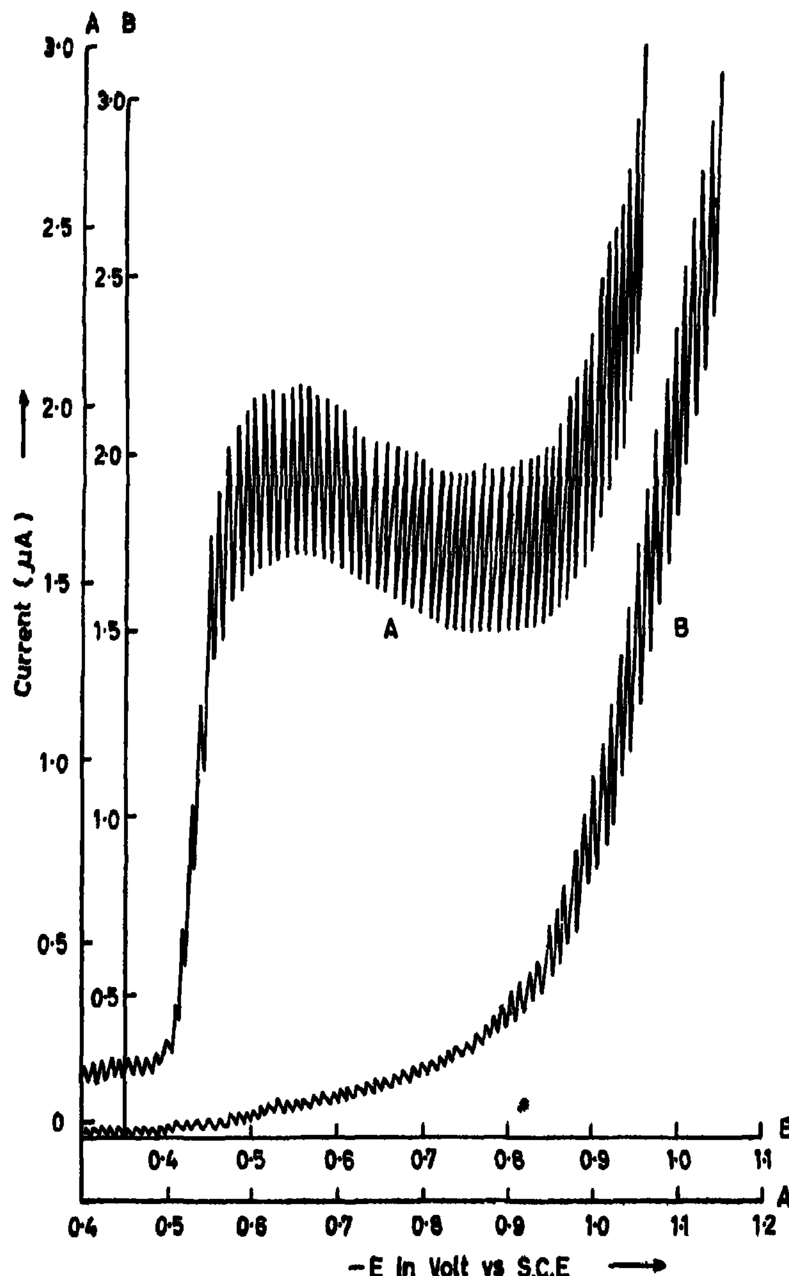


Fig. 3. Effect of salt-bridge on reduction of In(III) ($2 \times 10^{-4}M$) at pH 0.7, temp. 30° and $\mu = 0.1(NaClO_4)$. (A)—potassium chloride salt-bridge and (B)—sodium nitrate salt-bridge.

nitrate salt-bridge and potassium chloride salt-bridge. The Fig. 3 shows that at pH 0.7 the shapes of the waves are altogether different for the two salt-bridges. In presence of potassium chloride salt-bridge height of the first wave was considerably high with a faint minimum at nearly −0.6 to −0.8 V. The remarkable influence of potassium chloride salt-bridge may be due to leakage of traces of potassium chloride into the test solution.

The reduction behaviour of In(III) in presence of potassium chloride salt-bridge at different pH values is presented in Table 3. The results show that the potassium chloride salt-bridge has significant effect at low pH values. The half-wave potential observed at pH ⩾3 with potassium chloride salt-bridge was slightly higher compared to that obtained with sodium nitrate salt-bridge.

TABLE 3—EFFECT OF POTASSIUM CHLORIDE SALT-BRIDGE ON HALF-WAVE POTENTIAL AT DIFFERENT pH VALUES

pH	$-E_{\frac{1}{2}}$* (Volt)	Remarks
2.0 M Perchloric acid	0 95 (Second wave)	Only second irreversible wave was observed
0 45	0 516	Irreversible with minimum
	0 91 (Second wave)	Irreversible
0.80	0 527	Irreversible with minimum
1.00	0.527	Irreversible, minimum was absent
1 50	0 543	Irreversible
2 02	0.560	"
2.50	0.521	"
3.00	0.516	Reversible
3.20	0.517	Reversible

*Half-wave potential of first wave except otherwise stated.

Kinetic character of the waves: The ratios of the current at 58.5 cm (corrected) and 18.5 cm (corrected) of mercury height using sodium nitrate salt-bridge and potassium chloride salt-bridge have been given in Tables 4 and 5, respectively. The ratio is nearly equal to the theoretical value (1.78) at pH 3.0-3.3 but decreases on lowering the pH in both the cases. It was only 1.05 at pH 0.9 in the case of sodium nitrate salt-bridge indicating that the wave became kinetic-controlled at pH 0.9. However, the wave was partially kinetic-controlled at the same pH value when potassium chloride salt-bridge was used.

TABLE 4—EFFECT OF pH ON THE RATIO OF In(III) LIMITING CURRENTS AT 58.5 AND 18.5 cm MERCURY COLUMN AT 30°; μ=0 1 ($NaClO_4$)

Salt-bridge—Sodium nitrate

pH	0.90	1.10	1.50	2 60	3 10	3.28
Ratio	1 05	1.14	1.52	1.65	1.78	1.77

TABLE 5—EFFECT OF pH ON THE RATIO OF In(III) LIMITING CURRENTS AT 58.5 AND 18.5 cm MERCURY COLUMN AT 30° AND μ=0.1 ($NaClO_4$)

Salt-bridge—Potassium chloride

pH	0.80	0.90	1.50	2.50	3.10	3.30
Ratio	1.58	1.61	1.65	1.67	1.79	1.78

Role of potassium hydrogen phthalate: The effect of pH on the reduction of In(III) in the presence of phthalate is presented in the Table 6. These results show that the reduction of In(III) becomes reversible even at low pH values on addition of phthalate. The amount of phthalate required to make the wave reversible decreased on increasing the pH. The half-wave potential increased slightly on increasing the pH, but it remained nearly constant (−0 512 V) in the pH range 2 8−3.2. The wave was found to be diffusion controlled at pH 2.9−3.3.

TABLE 6—EFFECT OF POTASSIUM HYDROGEN PHTHALATE ON In(III) REDUCTION AT DIFFERENT pH VALUES

pH	Phthalate $M \times 10^6$	i_l (μA)	$-E_{\frac{1}{2}}$ Volt	Slope Volt
1.70	10	2.02 (1 09)	0.509	0.0225
2 44	5	2.17 (1.84)	0.510	0 0220
2 80	3	2 20 (2 04)	0.511	0.0215
3.02	3	2.23 (2.23)	0.512	0.0200
3.20	3	2.29 (2.29)	0.512	0.0210

Figures in parenthesis are of corresponding limiting current in the absence of phthalate.

Strizhov *et al*[27,28] have reported that phthalate acts as a catalyst in the reduction of In(III). It seems that the effect of phthalate in the present case may be due to the preferential adsorption of indium phthalate complex on the mercury drop, facilitating the reduction of In(III). Phthalate thus acts as a catalyst.

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About the Nature of M—S Bond in Complex Compounds

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COMPLEX formation can be interpreted as an acid base reaction, in which the metal acts as an acid and the ligand as a base. A linear relationship between the stability of the complexes of a metal ion and the base dissociation constants of the corresponding ligands, has also been shown[1]. This relationship should hold good in case of structurally related ligands. Literature[2] reveals that non-transition metals form more stable complexes with the ligands containing elements in the second period of a group as the coordinating atoms, whereas the ligands involving later elements of the group form less stable complexes. The reverse is, however, observed in case of transition metals. The relative stabilities of the complexes containing nitrogen, phosphorus and arsenic atoms have been worked out by Nyholm and coworkers[3]. Coates[4] observed that the strength of coordination of $X(Me)_2$ (X=O, S, Se or Te) to aluminium trimethyl is in the order of O>S>Se>Te, but the dialkyl sulphides and tellurides coordinate with Pd(II), Pt(II) and Hg(II) whereas others do not, indicating reverse order of stability (S>O). In the transition metal complexes Pettit and coworkers[5] observed that the silver complexes of phenylselenoacetic acid is more stable than the corresponding sulphur and oxygen analogous. There is, however, no uniform pattern of relative coordinating affinities of all ligand atoms for all acceptor molecules and ions, not even when only simple unidentate ligands of closely analogous structures (e. g PR_3, R_2S) are considered. The relative affinities seem to depend more on the acceptors concerned. It was observed that under comparable conditions the relative tendencies of the alkyls of the fifth and sixth group atoms to coordinate with trimethyl gallium are N>P>As>Sb and O>S>Se>Te but the order appears to be N<P>As>Sb and O<S>Se>Te towards Pt(II). Other similar divergent examples have been observed.

Inspite of this lack of uniformity some regular features have emerged[6] :

(i) There is generally a difference between the co-ordinating affinities of the first and the second element from each of the three groups of ligand atom in periodic table i. e. between nitrogen and phosphorus, oxygen and sulphur and fluorine and chlorine.

(ii) There are two classes of acceptors :

(A) those which form their stable complexes with the first ligand of each group i.e. with nitrogen and fluorine, and

(B) those which form their most stable complexes with the second or subsequent ligand atoms.

Class A consists of most metals in their common valency states. The tendency of the ligands to get bound with such acceptors is directly dependent on their basicities, except in the cases where steric and other factor bring interference. The acceptors of class B, are less in number and are situated in an area of more or less triangular shape in the central part of the periodic table

Pearson[7], on the basis of his independent observations, grouped the metals and ligands as hard and soft Lewis acids and bases, respectively. He observed that the hard acids have a greater tendency to combine with hard bases and vice versa Pearson's hard and soft acids correspond to metals with A and B character and hard and soft bases correspond to ligands containing earlier and later elements of a group, respectively

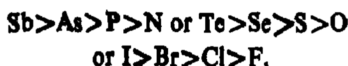
In view of the quantum mechanical concept of coordination, the class A or class B character of the metal ions is connected with the availability of d electrons and the electronegativity of the metal ion and π-bond formation.

An interpretation of π bonding has also been attempted in terms of molecular orbital theory. In normal mode of overlap, the T_{2g} orbitals of the metal ion do not find orbitals of the required symmetry on the ligand atom and hence remain as non-bonding molecular orbitals. In cases where the ligands have vacant $p\pi$ or $d\pi$ atomic orbitals on the ligand atom or the ligand molecules have vacant antibonding π molecular orbitals, they combine to form composite orbitals of the required symmetry to combine with the metal π orbital. π bonding and π antibonding molecular orbitals are thus formed. In terms of ligand field theory, the formation of π bonding and π-antibonding molecular orbitals increases the ligand field splitting, consequently increasing the stability of the complex.

Except in special cases (e.g. NO_2^-, 2,2'-dipyridyl, pyridine, CN^-, CO complexes where M-O or M-N $d\pi$-$p\pi$ interaction can take place)[8], oxygen and

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nitrogen have no π orbitals available to accept the electrons from the suitably placed d orbitals on the metal atoms. On the other hand sulphur and phosphorus have vacant d orbitals which can be used for $d\pi$-$p\pi$ bonding. Such π bonding is possible only with transition metals having electrons in d π orbitals. The conditions are most favourable with later transition metals in their normal oxidation states. Thus, for these metal ion complexes the stability increases in the order



Sb>As>P>N or Te>Se>S>O
or I>Br>Cl>F.

The extent to which such $M \rightarrow L$ π bonding occurs is difficult to assess, but the available evidence suggests that in favourable circumstances it does occur in the M-L bond in transition metal complexes with ligands containing phosphorous, arsenic and to a lesser extent in sulphur, selenium and tellurium containing ligands[9]. Nyholm and coworkers[8] observed greater stability of phosphine and arsine complexes compared to ammonia and explained it on the basis of the π interaction in M-P and M-As bonds.

Jorgensen[10] pointed out that soft base behaviour of sulphur containing ligands may not be due to the $M \rightarrow L$ π back bonding but may be due to polarization of sulphur by the metal ion. He has interpreted this in terms of charge transfer into continuum orbitals of the ligand. According to Klopman[11], in case of heteronuclear compounds with large difference in energies of the outermost orbitals of the reactants, very little electron transfer occurs and the interaction is ionic. However, if the difference in the energies of the interacting orbitals is small covalent bond formation takes place. The interaction of class B metals and soft base ligands, like sulphur containing ones belongs to the latter type while the bonding of class A metals with hard base ligands containing oxygen atoms are of the former type. The covalent interaction will definitely make the M-S bond stronger in case of class B type of metals.

Unfortunately ligands having sulphur, selenium and tellurium have been less extensively studied, although in recent years there has been considerable interest shown in sulphur containing ligands[12-18]. The stability constant of the complexes of several sulphur containing ligands have been measured. The stability constants of the metal complexes of thioglycollic acid, β-mercapto propionic acid, 2-amino ethane thiol and mercapto succinic acid have been determined[19]. Stabilities of uranyl chelates of hydroxy, mercapto and amino derivatives of acetic, propionic and salicylic acids fall in the order NH_2>OH>SH. Uranyl ion forms a stronger complex with glycollate than with thioglycollate ion[20]. This indicates class A behaviour of uranyl ion. Formation constants of the complexes of thioglycollic acid, thiolactic acid, thiosalicylic acid and their oxygen analogues with Ni(II), Zn(II), Cd(II), Mn(II) and Tl(I) have been studied[21-24]. We have also carried out the study of complexes with O and S containing anilides and acids and have shown that M-S interaction is stronger than M-O[25-26]. Allen and coworkers[27] have observed weak class B character of rhenium(II). Both Mn(II) and Re(II) are border line cases. Martin[28] also observed that the formation constants of mercapto acetamide complexes of Ni(II) and Mn(II) are in the order of Ni>Mn.

The stronger binding of sulphur with class B type of metal ions is of importance in biochemical processes. Fe^{2+} and Fe^{3+} have a high affinity for sulphur or nonheme iron sulphur proteins[29]. The first row transition metal ions are known to co-ordinate to cystine through NH_2 and S and carboxylate remains unco-ordinated[30]. Similarly penicillamide, -SC-CH_2-CH(NH_2) COO^-, also co-ordinates to transition metal ions through -NH_2 and S[31].

Gerlach and Holm[32] have carried out nmr studies of the β-amino thione and the corresponding oxygen compounds and indicated π interaction in the Ni-S bond. ESR studies of copper diethyl dithiocarbamate complex also indicated presence of Cu-S π bond[33]. Possibility of $M \rightarrow L$ π interaction has also been discussed in a recent review article by Pettit[9]. Nanjo and coworkers obtained the nmr spectrum of $Ni(EtOCSS^-)_2$ complex and observed shift in the ligand protons indicating that the unpaired electrons of Ni(II) are partially delocalized on the system of the ligand. Richards and Johnson[34] have also shown the possibility of $M \rightarrow S$ π interaction on the basis of Mossbauer studies on dicyano-1, 2-dithioethylene complex of Fe(III). The high magnitude of the isomer shift has been interpreted presumably as a consequence of the electron donation from the ligand orbitals to the metal d π orbitals with little contribution from back donation from metal orbital into empty ligand π orbitals. Bonamico and Dessy[35] carried out X-ray studies of complexes involving M-S and M-Se bonds and observed M-L bond distance to be shorter than a single bond. This indicates the formation of $M \rightarrow L$ π bonds. Further structural studies showing double bond character in M-S bond in solid complexes of class B metals are essential to finally establish the existence of π interaction.

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High Purity and Special Materials for Electronics

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During the last few decades electronics industry has been recording a phenomenal growth and development and in this process has expanded its need for a variety of ultrapure and special materials for various applications. This technological advancement in electronics industry is synchronised with the availability of the required materials in a state of very high purity. Special materials for specific applications in the electronics industry are the semiconductors, laser materials, luminescent materials, magnetic materials and dielectrics. This article is aimed at a general review of such special materials for the electronics industry.

IN the last few decades the scientific advancement and technological explosion have enhanced the need for a wide variety of synthetic materials. Electronics industry alone has expanded its need for a number of special materials In addition to the basic materials such as process materials, process chemicals, gases, solvents, surface protection and encapsulation materials, solders, alloys and fluxes which are common with other industries, although required in a higher state of purity, the electronics industry needs special materials for unique applications such as semiconductors, laser and luminescent materials.

TABLE 1—ELEMENTAL AND COMPOUND SEMICONDUCTORS

Material	Energy gap (EG) (eV)	Band structure	m p. (°C)	Electron mobility μ_e (M^2/V. sec)	Hole mobility μ_h (M^2/V sec)
Ge	0.72	Indirect	937	0.39	0.190
Si	1.10	-do-	1420	0.14	0.048
InP	1.27	Direct	1070	0.53	0.065
InAs	0.33	-do-	490	3.30	0.028
GaAs	1.38	-do-	1235	0.86	0.025
ZnS	3.60	-do-	1830	0.01	—
CdS	2.40	-do-	1750	0.03	—
GaP	2.24	Indirect			
$GaAs_{1-x}P_x$	1.44-2.26	Direct-Indirect			

Ever since the discovery of transistor a few decades ago there has been a rapid growth and increasing specializations in solid state science. The new materials, by virtue of the utilization of the electronic, magnetic and optical properties of solids in device making, are required to be in a state of very high purity, the impurities being at parts per million to parts per billion level. These materials have further brought into focus physical parameters such as size crystallinity, phases present and crystal quality. The synthesis of such sophisticated materials in ultrahigh purity calls for new techniques such as chemical vapour phase deposition, floating zone melting and suitable environmental conditions. Equally important to the synthesis of these materials is the quality control or the evaluation of the impurities. Modern analytical techniques such as neutron activation analysis, spark source mass spectrometry, emission spectroscopy have been employed for this purpose

Semiconductor materials

The electrical behaviour in solid state devices depends on careful control of impurities and impurity gradients in semiconductors(Table 1). This calls for ultra-high purity for the raw materials used in semiconductor technology which contain electrically active impurities at parts per billion level and which possess crystallographic perfection. The potential application of a semiconductor is to make use of the electrical and optical effects in solids as in transistors, thermistors, thermoelectric devices, photoelectric cells, solar battery, photo-conductive detectors, phosphors, light emitting diodes and lasers

Elemental semiconductor

The most widely used semiconductors are the two elements silicon and germanium both of which have diamond cubic structure. They came into prominence with the development of the first germanium transistor in 1946 and the first silicon transistor in 1954.. Today, silicon technology has made germanium technology almost obsolete due to the abundance of its raw materials in nature, the high temperature and low leakage characteristics possessed by silicon devices and the impact it has made in the field of microelectronics for the manufacture of integrated circuits.

Compound semiconductors

Elements of group IV, III-V, II-VI of the periodic table can be suitably combined to form compound semi-conductors which generally have the sphalerite or wurtzite structures that are closely related to the diamond cubic structure. Other semiconducting compounds are the group IV-VI and V-VI materials. Gallium arsenide is a

very important compound semiconductor. It finds application either in the pure state or as an alloy in the GaP-As system in varactor diodes, Gunn devices, light emitting diodes, injection lasers, photocathodes, high temperature rectifiers, transistor and solar cells. The current flow in n-type gallium arsenide at field strengths greater than 3 KV/cm gives rise to transverse electron oscillations termed as Gunn effect which is made use of in microwave communication. In this field gallium arsenide has the greatest scope as its conduction electrons have higher mobilities (8000, 3900 and 1600 cm^2/VS for GaAs, Ge and Si) and limiting velocities (2×10^7, 6×10^6 and 9×10^6 cm/sec for GaAs, Ge and Si) than the other principal semiconductors. Gallium arsenide devices now rely exclusively on epitaxial layers as the active material This growth of the multilayered structure is generally accomplished either by liquid phase epitaxy or vapour phase epitaxy.

Among the higher energy band gap semiconductors gallium phosphide is of considerable importance. This finds extensive application as LED in the visible region, as dynode material in place of the conventional Cu-Be alloy. Another important application of compound semiconductors is in infrared detectors. Both InSb and InAs are used for this purpose.

Laser materials

Higher power, new wavelengths, tunability, improved ruggedness, reliability, reproducibility, stability and lower prices have combined to bring lasers into daily use. The principle of laser action is 'stimulated emission' in which existing photons stimulate the production of more photons by interacting with excited electrons. Under conditions of thermal equilibrium the lower energy states are more populated than the higher ones and stimulated emission is negligible. A population inversion is therefore an essential condition for laser action.

Lasers are generally classified by the medium in which stimulated emission occurs Common types of lasers include gas, liquid, solid-state and semiconductor. In each case the physical medium acts as a support for an energy level system the population of which can be inverted by optical pumping, by carrier injection, by electric excitation or by energy released in a chemical reaction.

Solid state lasers (Table 2) are made with both crystalline and amorphous materials, usually in rod form, with excitation accompanied by optical pumping. In these lasers the 'host' comprises the major part of the laser material with the remaining 'active' material (from a fraction of a per cent to 2 per cent by weight) contributing to the lasing action. The most important consideration in selecting compounds for lasers is the size match of the dopant and the host lattice site. Substitution of a similar charged ion in a lattice is more desirable than to have defectors or charge compensators. The laser materials should be optically homogeneous and the crystalline materials must have a high degree of

TABLE 2—SOLID STATE LASER MATERIALS

Host Material	Active ion	Structure	Lasing wave length (μm at 77°K)	Method of preparation
Al_2O_3	Cr^{3+}	Corundum	0.6935	Verneuil
CaF_2	Nd^{3+}, Sm^{3+}, Dy^{3+}	Fluorite	1.06,0.708, 2 36	-do-
LaF_3	Pr^{3+}, Nd^{3+}	Tysonite	0 598,1.04	Czochralski
$CaWO_4$	Pr^{3+}, Nd^{3+}, Ho^{3+}	Scheelite	1.047,1.065, 2 046	-do-
$Y_3Al_5O_{12}$	Nd^{3+}, Ho^{3+}, Er^{3+}	Garnet	1.06,2.09, 1 645	Verneuil
	Tm^{3+}, Yb^{3+}		1.88,1.03	Czochralski

perfection with the impurities distributed uniformly. Most of the lattices so far used have been simple or mixed oxides and fluorides whose structures are related to those of ruby, fluorite, scheelite or garnet. The active ions which cause laser action are that of transition metals, lanthanides or actinides. The width of the emission line will be small if only the above ions are used. The widely used synthetic routes for the laser materials are the several melt-growth methods such as the Verneuil, Bridgman, Czochralski and zone melting techniques and also the technique of growth from solution in high melting fluxes like PbO, PbF_2, $BaO+B_2O_3$, $NaAlF_6$ and alkali earth tungstates. Ruby ($Al_2O_3 : Cr^{3+}$) was the first laser to be operated and remains a widely used material particularly for its output in the visible part of the spectrum The chromium ions (Cr^{3+}) occupy the aluminium sites and are the active centres, their energy levels being determined by the crystal-field splitting of the host lattices. In the case of a three-level system to which ruby belongs, a large pumping power is required for laser action, i.e. for population inversion which can be achieved at lower pumping powers if a four-level system is employed. The rare-earth ions provide energy levels that are needed for operation in the four-level mode. A number of lasers made from rare-earth doped crystals such as $CaWO_4$, $Y_3Al_5O_{12}$(YAG) and $YAlO_3$(YALO) have now been developed. Nd^{3+} doped YAG laser with emission at 1060 nm has been used to produce visible light at 530 nm by the use of a non-linear harmonic generator, namely, $Ba_2NaNb_5O_{15}$. It is easier to achieve optical homogeneity in glasses rather than in crystalline substances Further, glass as a host offers greater flexibility of size and shape. Nd-glass lasers are currently capable of generating 10^{-11} second pulses, with energies upto 1,000 joules. Limitation to further increases is in the damage threshold of the glass itself. Beam fluxes exceeding 20 to 40 joules per cm^2 will cause deterioration or complete destruction. Larger diameter rods or further development of face-pumped glass discs could result in productions of higher energies. Until the advent of the transversely excited high pressure gas laser, solid-state lasers were the only type to produce very high peak power in pulsed operation. Peak power is desirable in a number of applications such as plasma/fusion experiments, transmission over long distances, and in systems where nonlinear optical

elements such as frequency converters are used.

The internal efficiency of a GaAs electroluminescent junction is so high that it can be used for laser operation. The laser transitions in semiconductor lasers are associated with the band structure. Actual light emission is obtained at the interface of n and p type bands whenever the electrons and holes are driven into this band junction in a process known as carrier injection. Semiconductor laser materials are predominantly covalently bonded with tetrahedral coordination. A typical homojunction laser is made of a single crystal wafer of GaAs doped with tellurium and zinc to create a p-n junction. The emitted beam is at 904 nm for GaAs. Operation is pulsed, with peak powers upto 100 watts in a single device or 1 KW in an array. Although the emission is stimulated, these are not as directive nor as monochromatic as other laser types. Laser action in ternary compounds was first observed in $GaAs_{1-x}P_x$ crystals and the first laser diodes to operate in the visible region of the spectrum have been made from Ga-As-P alloys prepared by vapour-phase epitaxy The most recent additions to the semiconductor laser family are the heterostructure injection lasers which operate at room temperatures, are extremely small and are capable of being powered by dry cells.

Luminescent materials

Luminescence is the emission of optical radiation[4], -uv, visible or infrared, that is the direct result of the energy released during electronic transitions within a material. The luminescence arises from a two-step process in which electrons and holes are generated in concentrations greater than those statistically permitted at thermal equilibrium and a significant fraction of these undergo radiative recombination generating photons. The recombination process is very strongly characteristic of the physical and electrical properties of the material.

Energy can be converted into photons in a variety of ways - thermoluminescence, cathodoluminescence, photoluminescence, chemiluminescence and electroluminescence. The creation of light by fast electron bombardment which is exploited in the communication field, particularly TV, has drawn significant attention towards inorganic luminescent materials since they are most stable to withstand electron bombardment. Typical phosphors (Table 3) include sulphides, silicates, oxides and tungstates. Zinc sulphide is the basic material widely investigated and the best known group among luminescent materials. The commercial development of ZnS phosphors is based on empirical formulae for their preparation. These include the precipitation of the sulphide, the addition of small concentrations of impurity atoms such as Cu, Ag, Au or Mn as activators and the presence of an alkali halide as a flux. ZnS and CdS form a completely miscible system of salts that have sphalerite structure at low temperatures and change to Wurtzite structure above 600°. Light emission may be obtained at any wavelength by appropriate mixing of ZnS and CdS which have

TABLE 3—PHOSPHORS

Compound	Activator ion	Colour characteristics	Area of application
ZnS	Mn	Orange	TV
ZnS	Ag	Blue	
ZnS	Cu	Green	
YPO_4	Tb	Green	Cathode ray tubes
Y_2SiO_5	Tb	Green	
$Y_3Al_5O_{12}$	Ca	Green	
$NaTaO_3$	Tb	Green	
$Sr_5(PO_4)_3Cl$	Eu	Deep blue	
YVO_4, Y_2O_3, Y_2O_2S $Gd_2O_3, Gd_2O_2S,$	Eu	Red	TV
YVO_4	Dy		
La_2O_2S, Gd_2O_2S	Tb	X-ray green	X-ray screen
CaF_2	Eu		Scintillators

luminescence in the blue and infrared region respectively. Tungstate (Mg_2WO_5 : W) and phosphate [$3Ca_3(PO_4)_2CaF_2$: Sb : Mn] phosphors find application in fluorescent lamps.

Considerable amount of research has been directed in recent years towards the development of rare-earth based phosphors and the results show that these new phosphors surpass the conventional ones in several respects. The rare-earth based phosphors employing rare-earths as hosts, activators and sensitisers have found new domains of application, namely, X-ray technology, cathode ray tubes of new capability, fluorescent lamps and infrared emitting diodes. Particular mention should be made about the use of YVO_4:Eu phosphor in colour television and that of the oxysulphide phosphors viz. Gd_2O_2S:Tb and La_2O_2S:Tb in X-ray intensifying screens. As a combination of high luminosity and saturated red hue is desired in colour television, the YVO_4:Eu phosphor, by virtue of possessing these characteristics has gradually replaced the other conventional cathode ray phosphors. The oxysulphide phosphors, by virtue of possessing a high absorption power for X-rays, enable radiologists to get high quality X-ray pictures of patients and also substantially reduce the dosage received by the patients. Y, La, Gd and Lu have 2-6-1-2 outer electron shells ; and their 4f shells are either empty (Y and La), full (Lu) or contain the maximum number of unpaired electrons (Gd). Accordingly, they are optically neutral (contribute no colour) and can be used as bases for special purpose glasses. Their oxides are phosphor hosts ; since they fluoresce without visible colour.

The biggest step forward in the electronics industry since the transistor is the development of monolithic microcircuitry and in this area electroluminescent devices are playing a prominent role. The combination of semiconduction and luminescence is brought about by depositing phosphors on the surface of a semiconducting glass or glass with a semiconducting film on it, coating the phosphor screens with the conducting and reflecting films of aluminium and applying an electric field across the screen. A wide range of materials—ZnS, ZnSe, CdS,

CdSe, PbSe, PbTe, $GaAs_{1-x}P_x$, $Al_xGa_{1-x}P$, GaP, GaAs, InP, InAs, $BaTiO_3$, SiC, $CaWO_4$ and $ZnSiO_4$ have been found to exhibit electroluminescence. Much of the recent interest in the electroluminescent field has been in the area of light emitting diodes (LED).

Electroluminescent devices can be used as radiation sources in place of the tungsten filament lamps These are rugged, are operated in the cold, can be modulated at high speeds, can be made coherent and can operate at voltages compatible with transistor circuitry. As such, they find application in visual data displays and optical communication systems.

Recent trends in materials research

Considerable amount of activity has been directed in recent years towards the development of photochromic and cathodochromic materials, amorphous semiconductors, liquid crystals and magnetic bubble domain. Photochromic materials have the property of changing colour under light illumination. Photochromic materials under investigation are the rare earth doped CaF_2 and transition metal doped calcium and strontium titanates and they are being tried for application in optical memories for computers and in glasses for achieving variable transmittance. A wide variety of amorphous materials—PbO, CuO, Fe_2O_3, V_2O_5, HgO, Cu_2O, Al_2O_3, Ta_2O_5, Se. GaP, ZnS, As_2Se_3—have been found to exhibit transition from a normal high resistance state to a low resistance state in times of the order of microseconds when subjected to a threshold voltage. Memory switches based on this phenomena are under development.

Liquid crystals are organic substances which simultaneously exhibit properties of both liquids and solids over very narrow and specific temperature ranges. There are three types of mesomorphic states — smectic, nematic and chlolestric. The last two categories have optical properties which can be made use of in providing a radically new way of converting electrical, thermal and mechanical signals into coloured viewing patterns. Magnetic bubbles, a new way of storing, manipulating and retrieving digital information, offer tremendous potential for improving the logic, memory, counting and switching processes associated with communication systems. They provide information storage at a density of greater than 10^6 bits per square inch and information processing at rates of 1 million bits per second. The central element of a magnetic bubble device requires single crystals of materials with unique magnetic properties that will sustain small bubble like magnetic regions which can move at high velocity. The substituted garnets appear to provide a technological solution to the materials requirement for the bubble domain memory.

Electronic grade purity specifications are absolutely essential since minor amounts of impurities can drastically alter the physical properties of the materials, thereby resulting in undesired device performance. These factors naturally called for major efforts in developing the process know-how and over the last few years significant advances have been made in this direction.

By and large purification by a single present day method seldom gives the desired purity and, therefore, a combination of methods is sought. For example, in the final purification by zone melting it is imperative that the starting material should already be sufficiently pure, i. e. 99.9% or better, failing which, even under the most favourable experimental conditions either the desired purity is not achieved or the yield of such a product is low. In such cases, as stated earlier, bulk of the impurities can be removed by preliminary chemical or physico-chemical processes prior to zone refining. Equally important for effective removal of impurities is the specificity of the method employed. Both vapour phase and liquid phase epitaxy techniques are employed for the growth of multilayered structure. Gallium arsenide devices now rely exclusively on epitaxial layers as the active material. The reproducible growth of thin layers with the necessary dimensional control is difficult by the above techniques. The advantage, however, is not necessarily dimensional precision, but the high quality of the semiconductor layers. There is another growth technique called molecular beam epitaxy that permits better precision in layer thickness control. The methods normally used for the growth of single crystals are the melt-growth ones such as the Verneuil, Bridgman, Czochralski and zone techniques.

The evaluation of impurities in the processed materials which will determine their (materials) end use requires the development of sophisticated analytical techniques to determine impurities at parts per billion level.

Status of developing special materials for use in electronics industry in India

Until recently the country's requirements of electronic materials have been largely met by imports. The compelling necessity for developing indigenous process and primary materials for electronics industries in the country and, thereby, becoming self-reliant in this field was realised. Accordingly a committee was set-up under the chairmanship of late Dr. H. J. Bhabha which published a report "Electronics in India" in 1966. This report not only emphasised but also quantified the special materials requirement for the electronics industries in the country and also gave a fillip to research and development work on various primary materials in the country. Research and Development programmes were initiated in some laboratories, namely, B.A.R.C., Trombay, N.P.L., Delhi, S.S.P.L., Delhi, N.C.L., Poona, N.A.L., Bangalore and these efforts have started taking definite shape. Based on the process knowhow for various high purity materials developed at Chemistry Division, B.A.R.C., Trombay, a Special Materials Plant has been set up at the Nuclear Fuel Complex, Hyderabad, where a number of high purity materials

which include antimony, arsenic, bismuth, boron tribromide, cadmium, gallium, gold, indium, lead, phosphorous oxychloride, selenium, silver, tin, tellurium, tantalum, zinc etc. are already in production.

The complexities involved in the synthesis, evaluation and utilisation of the sophisticated materials and the rate at which yesterday's innovations are becoming obsolete today in the electronics industry, any materials development programme should be broad-based in line with the growth of electronics in the country in general.

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Electrophilic Substitution in Indoles. Part-I : Reaction of 3-Methyl Indole with Sulphuryl Chloride[§]

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Skatole (I) on treatment with sulphuryl chloride in presence of acetic acid underwent interesting substitution and rearrangement reactions to afford four new oxindole compounds, 3,5,7-trichloro-3-methyl oxindole (II), 3,5-dichloro-3-methyl oxindole (III), 3-hydroxy-5,7-dichloro-3-methyl oxindole (IV) and 3-hydroxy-5-chloro-3-methyl oxindole (V)

IN continuation of our work[1-3] on the electrophilic substitution of indoles we studied the reaction of 3-methyl indole (skatole) with sulphuryl chloride in acetic acid. Substitution reactions and interesting rearrangements were observed.

Acheson *et al*[4] had earlier reported the formation of ethyl-3-methyl oxindole-3-carboxylate from ethyl-3-methyl-indole-2-carboxylate by the action of sulphuryl chloride in acetic acid. No chlorine atom was incorporated in the aromatic nucleus or in the pyrrole ring. However, we found that skatole (I) under similar conditions underwent substitution with chlorine both on the aromatic nucleus and the pyrrole ring yielding products (II–V). The products could be successfully resolved into pure components on Tswett column (over silica gel).

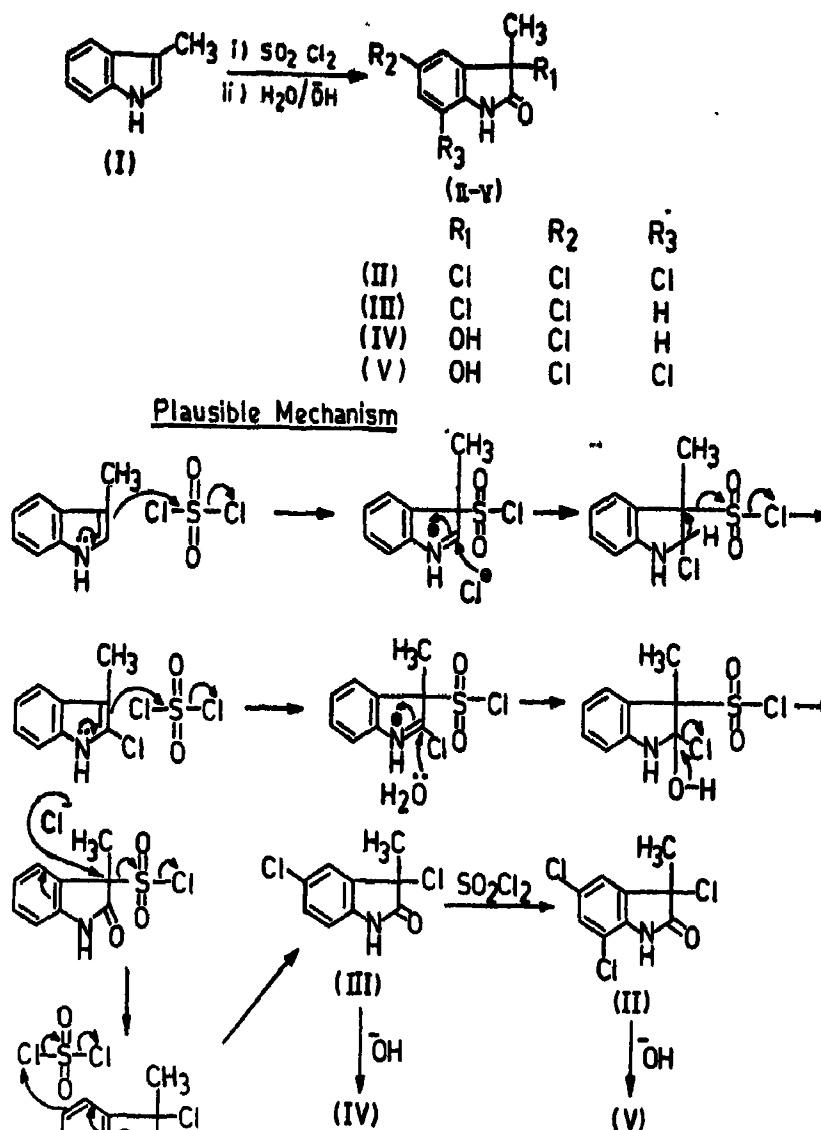
Compound (II), $C_9H_6NOCl_3$, m.p. 160° (petrol : benzene=1 : 1), showed three molecular ion peaks at M^+ 253, 251 and 249 corresponding to the isotopic chlorine atoms. The ^1H nmr spectrum (d_6-acetone) of II exhibited chemical shifts at δ7.48 (d, 1H, Jm=1.9 Hz) for the C_4-H, δ7 37 (d, 1H, Jm=1.9 Hz) for C_6-H, δ1.85 (s, 3H) for the methyl protons at C_3 and δ10.06 (1H, disappearing on deuteration) for indole >N*H* The electronic spectra displayed significant light absorption at 264 (log ϵ=3.88) and 315 nm (3.24), the latter being characteristic of a chlorine substituted aromatic nucleus. The structure could therefore be established as 3,5,7-trichloro-3-methyl oxindole (II).

The compound (III), $C_9H_7NOCl_2$, m.p. 150° (petrol : benzene=1 : 2) showed two molecular ion peaks at M^+ 215 and 217 due to the presence of chlorine atom in the molecule. Strong absorption peaks were observed in the electronic spectra at 311 (log ϵ=3.07), 260 (3.87) and 218 nm (4.92). The ^1H nmr spectrum (d_6-DMSO) confirmed the structure of this compound (III) as 3,5-dichloro-3-methyl oxindole. While aromatic C_4-*H* proton resonated at δ7.54 (d, 1H, Jm=2 12 Hz), the other two aromatic protons at C_6 and C_7 were discernible at δ7 28 (dd, 1H, Jo=8.29, Jm=2.12 Hz) and δ6 87 (d, 1H, Jo=8 29 Hz) respectively. The C_3-methyl protons were observed at δ1.79 (s, 3H) and the >N*H* proton appeared at δ10 88 as a singlet which disappeared on deuteration.

Compound (IV), $C_9H_6NO_2Cl$ (M^+ 197 and 199), m.p. 240° (ethylacetate : benzene=3 : 1) was characterised as 3-hydroxy-5-chloro-3-methyl oxindole from its spectral data. The electronic spectrum showed absorption maxima at 313 (log ϵ=4.15), 298 (3 09) and 258 nm (3.93) characteristic of a chlorinated oxindole compound. The ^1H nmr spectrum, when recorded in d_6-DMSO, also substantiated this observation. Characteristic peaks were discernible in the ^1H nmr spectrum at δ7.28 (dd, 1H, Jm=2 2, Jp=0 4 Hz ; C_4-H), δ 7.21 (dd, 1H, Jo=9 0, Jm=2 2 Hz, C_6-H). δ6 78 (dd, 1H, Jo=9 0, Jp=0 4 Hz, C_7-H), δ1.33 (s, 3H, C_3-CH_3), δ10 29 (s, 1H, >N*H*, disappearing on deuteration) and δ5.95 (s, 1H, C_3-O*H* exchangeable with D_2O).

The compound (V), $C_9H_7NO_2Cl_2$(M^+ 231 and 233), m.p. 225° (benzene : ethyl acetate=4 : 1), λ_{max} in nm · 304 (log ϵ=3.17), 259 (3 94) and 216 (4.31), was characterised as 3-hydroxy-5,7-dichloro-3-methyl oxindole. The ^1H nmr (d_6-DMSO) showed characteristic signals for the C_6-H at δ 7 38 (d, 1H, Jm=1.75 Hz), C_4-H at δ7.30 (d, 1H, Jm=1.75 Hz), C_3-CH_3 at δ1.36 (s, 3H) and an exchangeable proton at δ10 78 for >N*H* (s, 1H). Unfortunately the C_3-hydroxyl proton could not be detected, possibly it underwent deuteration in d_6-DMSO. The presence of C_3-OH in the compound (V) could be confirmed from mass spectrum and ^{13}C nmr spectrum analysis.

§Dedicated to Professor N. R. Dhar on the occasion of his 90th birthday.



Scheme 1

TABLE 1—^{13}C nmr SPECTRA OF THE COMPOUND II-V

Carbon Numbers	Compound Numbers [Chemical Shifts in ppm (δ)] (II)[b]	(III)[c]	(IV)[c]	(V)[c]
C-2	175.23 (s)	174 48 (s)	180 59 (s)	179 51 (s)
C-3	61 94 (s)	62 49 (s)	74 06 (s)	73.52 (s)
C-4	122.91 (d)	124 31 (d)	124 94 (d)	122.50 (d)
C-5	133 60 (s)	132 74 (s)	136 92 (s)	138 02 (s)
C-6	129.69[d] (d)	130 02[e] (d)	129 94 (d)	128.00 (d)
C-7	116.32 (s)	111 80 (d)	112.32 (d)	114.92 (s)
C-4a	129 04[d] (s)	126 49[e] (s)	127 03 (s)	126 51 (s)
C-7a	135 90 (s)	139 44 (s)	141 29 (s)	136.93 (s)
C_3-CH_3	25 56 (q)	24 65 (q)	25.47 (q)	26.05 (q)

b : $CDCl_3$; δ($CDCl_3$) = δ(TMS) + 76.9
c : d_6-DMSO ; δ(d_6-DMSO) = δ(TMS) + 39.5
d, e : values are interchangeable.

The structures of all these products have been confirmed from their ^{13}C nmr spectra (both SFORD and noise decoupled) and the plausible mechanism of their formation has been rationalised in Scheme 1.

Experimental

Melting points were recorded in a Köfler Block and are uncorrected. The uv spectra (95% aldehyde free ethanol)[9] were recorded on a Varian Techtron 634 spectrophotometer, the ir spectra on a Beckman IR 20 spectrometer in KBr disc, the ^{1}H nmr (80 MHz, Internal standard : TMS) and ^{13}C nmr (20 MHz) spectra were run on Varian CFT-20 and Varian FT-80A spectrophotometer. The column chromatography was carried out with silica gel (B.D.H., 60-120 mesh) and thin-layer chromato-

graphy was run using silica gel (Gouri Chemicals, Calcutta). The organic solvents were dried by using appropriate drying agents and the samples were routinely dried over P_2O_5 for 24 hr.

Preparation and isolation of 3,5,7-trichloro-3-methyl oxindole (II), *3,5-dichloro-3-methyl oxindole* (III), *3-hydroxy-5-chloro-3-methyl oxindole* (IV) *and 3-hydroxy-5,7-dichloro-3-methyl oxindole* (V) : 3-Methyl indole (skatole) (5 g ; 0.0427 mole) was dissolved in acetic acid (50 ml) and the mixture was warmed on a water bath until the solid dissolved. The solution was then heated to 50-60° and stirred while a mixture of SO_2Cl_2 (14 ml) in acetic acid (28 ml) was added fairly rapidly from the dropping funnel. When the addition was complete, the reaction mixture was heated to 70° and kept at this temperature for 30 min. The mixture was allowed to cool slowly with stirring and left for 36 hr at room temperature. The reaction mixture was poured into ice-water, the *p*H being maintained at 5 by dropwise addition of about 4*N* NaOH solution. The remaining acid was neutralised with $NaHCO_3$. The mixture was extracted with ether, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated to yield a dark brown mass which on chromatography over silica gel with solvents of increasing polarity (petrol, benzene and ethylacetate in various proportions) afforded four compounds.

The compound (II) was obtained in the petroleum-benzene (1 : 1) and benzene eluates, m.p. 160° (petrol : benzene=1 : 1), yield 21%, ν_{max}^{KBr} : 3100 (>NH), 1730 (>CO), 1610, 1580 and 1450 cm^{-1} (aromatic), m/e : 253, 251, 249, 214 (base peak), 187, 179, 151, 123, 114, 89, 76, 63 and 52.

Further elution with benzene afforded the product (III) in crude form. It was subsequently purified by rechromatography over silica gel using benzene-ethylacetate, 5 : 1, m.p. 150°, yield 4.5%, ν_{max}^{KBr} : 3200 (>NH), 1760, 1700 (>CO), 1625 and 1485 cm^{-1} (aromatic), m/e : 217, 215, 180 (base peak), 162, 145, 117, 89, 62, 58.

The compound (IV) was obtained from the benzene-ethylacetate, 3 : 1 eluate and purified by repeated crystallisation, m.p. 240°, yield 15.2%, ν_{max}^{KBr} : 3200 (>NH/-OH), 1695 (>CO), 1610 and 1470 (aromatic) The compound under electron impact showed two molecular ions at m/e 199 and 197. Further fragmentation yielded particles having m/e at 182, 171, 169, 156, 154 (base peak), 126, 99, 90, 63 and 43.

The mother liquor of the compound (IV) upon chromatography over silica gel afforded the compound (V) in the benzene : ethylacetate, 4 : 1 eluate, m.p. 225° (benzene : ethylacetate, 4 : 1), (yield 0.7%), ν_{max}^{KBr} : 3370 (>NH), 3160 (-OH), 1610 and 1450 cm^{-1} (aromatic). The mass spectrum showed two molecular ions at m/e 233, 231 respectively, other ion fragments being at m/e 205, 203, 190, 188, 160, 124, 97, 62, 61, 43 (base peak).

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Structural Studies of a New Flavone Glycoside from the Seeds of *Cassia nodosa*

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IN an earlier communication[1] isolation of anthraquinone and flavone glycosides from the seeds of *Cassia nodosa* and the structural studies of the anthraquinone glycosides had been reported. The present report deals with the structural studies of the flavone glycoside

The flavone glycoside, $C_{23}H_{24}O_{10}$, when hydrolysed with ethanolic hydrochloric acid, gave rhamnose (PC, osazone) and an aglycone $C_{17}H_{14}O_{6}$. On the basis of standard colour reactions[2] and spectral data[3,4] and chemical degradation studies, the aglycone has been identified as 5,4'-dihydroxy 7,3'-dimethoxy flavone (velutin).

The aglycone showed bathochromic shift with aluminium chloride but the glycoside did not, indicating thereby that the rhamnose molecule is attached to the hydroxyl group at position 5. On periodate oxidation two moles of periodate per mole of the glycoside were consumed producing one mole of formic acid which showed that the sugar rhamnose is in the pyranose form. The hydrolysability of the glycoside by Taka diastase showed the presence of α-linkage.

The aglycone, velutin, had been reported earlier from some plant sources[5] but the glycoside is a new one, being reported for the first time.

Experimental

Isolation and purification of the glycoside has been described in an earlier communication[1]. Glycoside, m.p. 138°; Found C, 60.02; H, 5 99 Calcd. for $C_{23}H_{24}O_{10}$; C, 60 00; H, 6 00%. UV λ_{max}^{EtOH} 265, 345; $+AlCl_3$ 280, 350; +NaOEt 290, 398 nm; ir ν_{max}^{KBr} 3440, 2950, 2880, 1185, 1605, 847, 730, 720 cm^{-1}, nmr (DMSO) δ : 3.90 (s, 6H, OCH_3); 4.20 (s, 1H, H-1" rhamnosyl); 3.50-4.00 (br, 4H, sugar protons); 6.38 (d, J=2.5 Hz, 1H, C-6); 6 75 (d, J=2.5 Hz, 1H, C-8); 6.88 (s, 1H, C-8); 7.02 (d, J=8.5 Hz, 1H, C-5'), 7.60 (dd, J=2.5, 8.5 Hz, 2H, C-2', C-6').

Hydrolysis: The glycoside (200 mg) was hydrolysed using 7% ethanolic hydrochloric acid (25 ml) under reflux for 6 hr, ethanol distilled off and the aglycone crystallised from ethyl acetate, m.p. 225° (C, 64 70; H, 4.70, Calcd for $C_{17}H_{14}O_6$; C, 65.00; H=4 50%). Acetate: (Ac_2O/Py) m p. 207°, acetyl percentage, found: 20; calcd. for $C_{17}H_{12}O_6(COCH_3)_2$; 21.60. Methyl ether: ($Me_2SO_4/K_2CO_3$) m.p. 192°, methoxyl percentage, found 32 92; calcd. for $C_{15}H_6O_2(OCH_3)_4$; 36.26). UV λ_{max}^{EtOH}: 268, 348; $+AlCl_3$ 268, 383; +NaOEt 293, 398 nm; ir ν_{max}^{KBr}: 3440, 2950, 2850, 1180, 1660, 1605, 845 cm^{-1}; nmr(DMSO) δ : 3.85 (s, 3H, OCH_3); 3.92 (s, 3H, OCH_3); 6.35 (d, J=2.5, 1H, C-6); 6.75 (d, J=2.5 Hz, 1H, C-8); 6.90 (s, 1H, C-3); 7.01 (d, J=8 5 Hz, 1H, C-5); 7.60 (dd, J=2 5 Hz and 8.5 Hz, C-2', C-6').

Periodate oxidation: The glycoside (20 mg) was dissolved in ethanol (25 ml) and distilled water (25 ml), treated with 0.1 *M* sodium *meta*-periodate (25 ml) and the reaction mixture allowed to stand for 48 hr. The amounts of periodate consumed and formic acid liberated were estimated by titrimetric method of Hirst and Jones[6]. For each mole of the glycoside, 1.8 mole of periodate was consumed and 1.2 mole of formic acid liberated

Enzymic hydrolysis: The glycoside was hydrolysed using Taka diastase at 25-30° for three days when L(−)-rhamnose was found in the hydrolysate (PC).

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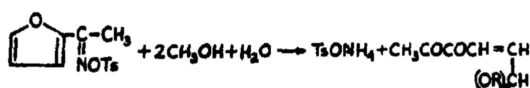
Rearrangement in Furyl-2-Keto-Oximes

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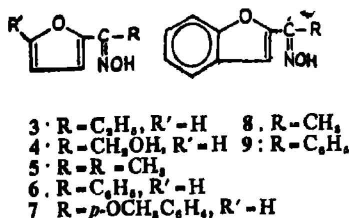
Solvolytic rearrangement of tosylates of benzofuryl - 2 - alkyl(aryl)ketoximes, 3-alkyl (aryl) benzofuryl-2-alkyl ketoximes and 2-substituted (and unsubstituted) benzofuryl-2-alkyl ketoximes with aqueous methanol depends upon their configurations Tosylates of *syn*-benzofuryl-2-alkyl ketoximes remain unchanged while *syn*-benzofuryl-2-aryl ketoxime tosylates undergo Beckmann rearrangement to yield benzofuran-2-carboxylic acid anilides. *anti*-Benzofuryl-2-alkyl (aryl) ketoximes afford three types of compounds, namely, (a) coumaran-2-one, (b) chromonols and (c) neutral products which are mixtures of diastereoisomers and assigned a chroman-3-one (and not a chroman-4-one) structure.

IN course of synthesis of aminofuran derivatives by following the procedure adopted by Neber[1], Vargha *et al*[2] quite surprisingly obtained *cis*-4, 5-dioxo-2-hexenal dimethyl acetal (2) by the solvolysis of the tosylate of furyl-2-methyl ketoxime (1) as in Scheme 1.



Tosylate of (1) Scheme 1

On attempted extension of the investigation[3,4] with other furyl ketoximes (3) to (9), uniform results were not obtained. Thus, the reaction of tosylate (4) with aqueous alcohol occurred as in Scheme 1, but the tosylates of (3) and (5) remained unchanged while tosylates of aryl ketoximes (6) and (7) underwent Beckmann rearrangement with the formation of the corresponding furan-2-carboxylic acid anilides and *p*-toluenesulphonic acid.



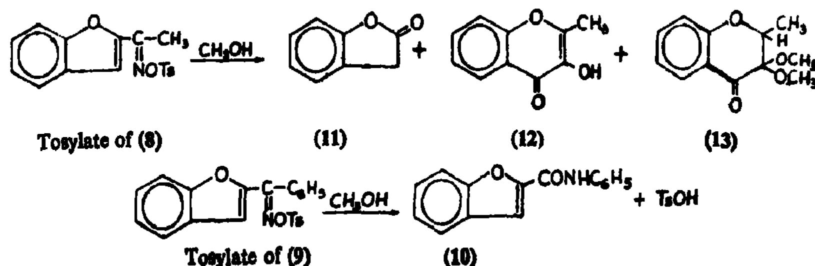
3 · $R = C_6H_5$, $R' = H$ 8 . $R = CH_3$
4 · $R = CH_2OH$, $R' = H$ 9 : $R = C_6H_5$
5 · $R = R' = CH_3$
6 . $R = C_6H_5$, $R' = H$
7 $R = p\text{-}OCH_3C_6H_4$, $R' = H$

In the benzofuran series, the solvolysis of tosylates of (8) and (9), however proved even more interesting and the results may be summarised in the Scheme 2.

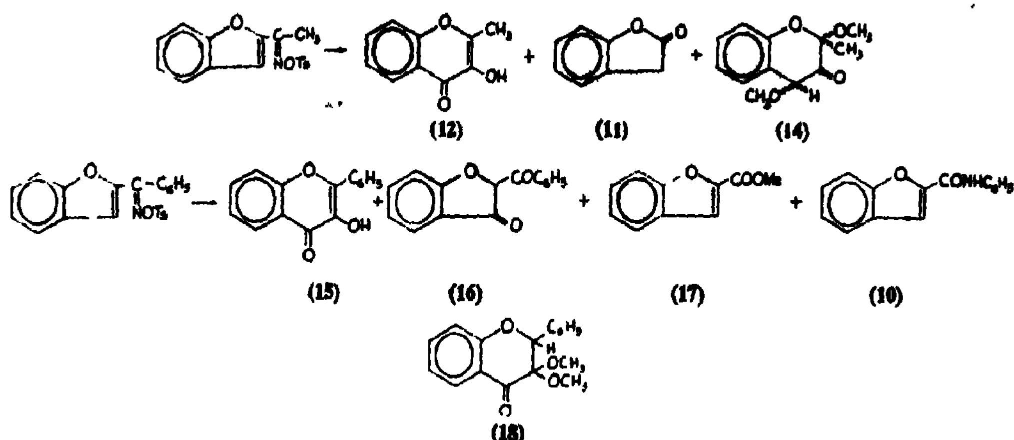
A neutral product derived from (8) was assigned structure (13) (2-methylchroman-4-one-3-dimethyl acetal) on the basis of analytical data and conversion of its oxime into 2-methylchromonol-3 (12).

Geissman and Armen[5] re-examined the solvolysis of the tosylates of (8) and (9) and reported the isolation of the same three products including the neutral product which they formulated as (14) from tosylate of (8). The tosylate of (9), however, afforded (15), (16), (17) and (10) including *p*-toluenesulphonic acid but a compound analogous to (14) was not obtained in this case. The conversions are given in Scheme 3.

These authors assigned the structure (14) (2-methyl-2, 4-dimethoxychroman-3-one) to the neutral product and disputed the structure (13) assigned to it earlier. Structure (14) was based on the uv data and formation of 2-methylbenzo[b]furan-3-carboxylic acid on 48% HBr treatment. The evidence through uv spectrum in favour of chroman-3-one structure is based on the facts that the uv absorption spectrum of the neutral compound was found to bear a very close resemblance to that of *o*-cresol and lacked intense band absorption at λ_{max} 306 nm that characterises *o*-methoxyacetophenone. The oxime of the acetal (neutral product) showed an uv absorption spectrum almost identical with that of

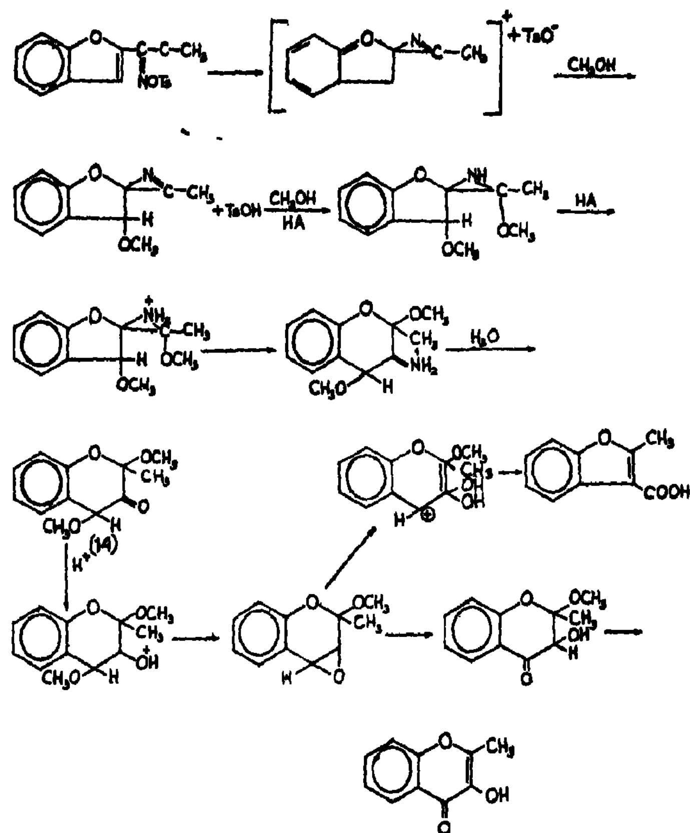


Scheme 2



Scheme 3

acetal itself indicating that the carbonyl group is remote from the aromatic nucleus. These workers considered the mechanism given by Vargha *et al*[8] for the formation of (12) as improbable and put forward a mechanism as shown below.



In order to explain these differences in the nature of product Vargha [6,7] pointed out that the geometrical configuration of the oximes could be the determining factor in the course of reaction and they sought to explain these differences accordingly. Thus, they[8] prepared the *syn*- and *anti*-isomers of ketoximes (1), (3), (5), (6), (8) and (9). Of the two possible isomers of these ketoximes one had been described in the literature, whereas only (5) and (6) were found to be a mixture of both *syn*- and *anti*-isomers. The isomerisations *anti*→*syn* were effected with hydrogen chloride. The configurations were determined by classical approach i.e. by identification of Beckmann rearrangement products and by careful study of the uv spectrum.

Simple *anti*-furyl-2-alkyl ketoximes give single intense absorption band at 270 nm. Furyl-2-phenyl ketoxime shows bands at approximately 240 and 270 nm. Only small changes were produced by isomerisation. *syn*-Furyl ketoximes were found to

absorb at somewhat shorter wavelength than their *anti*-isomers in agreement with the general rule.

syn-Furyl ketoximes give higher extinction values than the corresponding *anti*-isomers. These differences in extinction value were explained in terms of S-*cis* and S-*trans* conformations. The conjugated double bonds of the mentioned oximes may lie in the same plane either in an S-*cis* or in an S-*trans* conformation. According to Mulliken[5],



the bands of conjugated double bonds possess higher intensities in S-*trans* positions than in S-*cis* ones. When no steric hindrance exists, the ratio of both conformations of the compound is, in general, equal, although the S-*trans* modification appears to be somewhat more stable. Studies carried out with Stuart-Briegleb[6] models showed that certain equilibrium may take place between both conformations in the case of *anti*-furylketoximes. *syn*-Furyl isomers, on the contrary, may only exist in an S-*trans* conformation, because of steric hindrance.

The intensity of the absorption bands of *anti*-furyl isomers consisting of both the conformations will range naturally below that of *syn*-furyl compounds of the predominantly S-*trans* conformation.

A reinvestigation[7] of the solvolysis reaction with the tosylates of *syn*- and *anti*- forms of the above furo-ketoximes separately showed that :

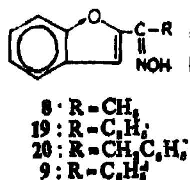
(i) Tosylates of the *syn*-furyl-alkyl ketoximes remained unchanged or resinified on prolonged heating.

(ii) Tosylates of the *syn*-furyl-alkyl ketoximes underwent Beckmann rearrangement to yield furan-2-carboxanilide.

(iii) Tosylates of the *anti*-furyl-alkyl (aryl) ketoximes afforded, in general, acetals of the reactive unsaturated trioxo compounds with opening of the furan ring. An exception to this finding was the tosylate of *anti*-5 - methyl furyl - 2 - methyl ketoxime where levulinic acid was obtained in place of acetal as a result of Beckmann rearrangement.

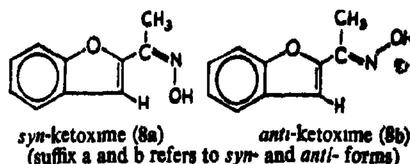
The conclusions derived by chemical method (from solvolytic experiments) were in agreement with the results of spectroscopic investigations.

In the benzofuran series the configurations of oximes were also studied in the light of pmr spectrum. *syn*- and *anti*-isomers of the ketoximes (19) to (22) were prepared. The pmr spectrum[12] of



8 : $R = CH_3$
19 : $R = C_2H_5$
20 : $R = CH_2C_6H_5$
9 : $R = C_6H_5$

syn-ketoxime (8a) exhibited a singlet at τ 2.14 for the proton at position 3, whereas the same proton appeared at τ 3.00 in *anti*-ketoxime (8b). This may be attributed to the neighbouring group (-OH) effect in *syn*-configuration as illustrated below :



syn-ketoxime (8a) *anti*-ketoxime (8b)
(suffix a and b refers to *syn*- and *anti*- forms)

The proton at 3-position in *anti*-ketoxime[12] (9b) appeared at higher field (τ 3.4) probably due to anisotropic effect of phenyl group as a result of rotation round C-C bond. The pmr spectra of *syn*- and *anti*-isomers of the ketoximes (19) and (20) revealed the same pattern. Benson and Pohland[13] made similar correlations in a series of oximes of substituted dimedones

Vargha *et al*[10] showed that in the benzofuran series tosylates of *syn*-ketoxime (8) remained unchanged and the rearrangement products as reported[8,9] earlier were obtained from the *anti*-isomers. The oxime (9) used by Geissman was shown to be a mixture of *syn*- and *anti*-isomers. *anti*-Benzofuryl-2-phenyl ketoxime, m.p. 156° and *syn*-benzofuryl-2-phenyl ketoxime, m.p. 145° were separated from oxime mixture, m.p. 132-33°. The compounds (10) and (17) in addition to TsOH were obtained from the solvolysis of tosylate of *syn*-ketoxime (9), whereas *anti*-tosylates afforded three crystalline products (15), (16) and (18) including NH_4OTs. Vargha *et al* however continued to hold the opinion that the neutral product had a chroman-4-one structure. Vargha's structure* has been adopted in a recently published book[11].

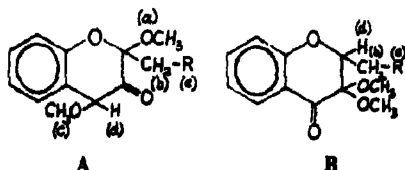
Surprisingly, no spectroscopic evidence other than the use of uv spectra was forwarded by any of the two groups of workers to establish the structure of the neutral product. The entire work in the benzofuran series was reinvestigated by Chatterjea *et al*[16] with a view to throwing more light on the nature of the neutral products derived from *anti*-ketoximes.

The neutral product derived from (8) showed carbonyl absorption at 1730 cm^{-1}. The infrared absorption value[14,15] is too high to be compatible with chroman-4-one structure but is consistent with a chroman-3-one structure. The pmr spectrum accounted not only for the chroman-3-one structure but showed the compound to be a mixture of diastereoisomers The ratio of diastereoisomers in the mixture (14) estimated on the basis of relative integral values of methyl and methoxyl protons are in the ratio of 56 : 44.

For adoption of structure A or B, the position of signals due to the isolated proton (b) and (d) in the pmr spectrum was of diagnostic value as these are in different magnetic environments. The other protons, namely (a), (c) and (e) in such a situation would be of little value for structural distinction. In structure A, the proton (d) is highly deshielded as

* A different structure suggested by Varga *et al*[17] has come to our notice. Earlier, the structure was considered and discarded by Geissman and Armen[8].

indeed is the case, τ 5.3 (s, 1H). Further, the proton (d) in B would be expected to be coupled by adjacent protons (b) and *vice-versa*. The protons (b) appear as a singlet at τ 7.6 (s, 3H) when R=H. The pmr spectra of the neutral products (21) to (23) and one isomer of (22) and (23) showed also sharp singlets at about τ 5.3 for the proton (d).

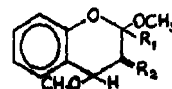


The mass spectra of pure diastereoisomers (22) and (23) is consistent with chroman-3-one structures[18].

TLC also indicated the neutral product from (8) to be a mixture and one diastereoisomer was separated only in pure form by repeated column chromatography (alumina) and homogenity of the pure isomer determined by pmr spectroscopy. This isomer on oximation afforded a pure oxime, m.p. 156-57° (*vide supra*).

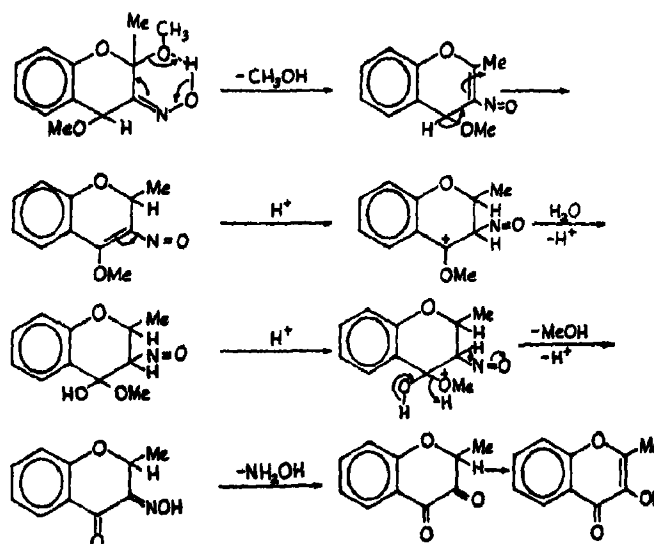
Analogous experiments with tosylates of *anti*-benzofuryl-2-ethyl ketoximes (19), benzofuryl-2-benzyl ketoxime (20) and benzofuryl-2-phenyl ketoxime (9) have been carried out by Chatterjea *et al*[16]. The tosylates of *anti*-ketoximes (19) and (20) reacted with aqueous methanol in similar way as tosylate of *anti*-benzofuryl-2-methyl ketoxime (8) and afforded similar sets of three products in addition to NH_4OTs. The neutral products may be formulated as (21) to (23).

Neutral products



21: $R_1 = C_2H_5$, $R_2 = O$
22: $R_1 = CH_2C_6H_5$, $R_2 = O$
23: $R_1 = C_6H_5$, $R_2 = O$
24: $R_1 = CH_3$, $R_2 = NOH$
25: $R_1 = C_2H_5$, $R_2 = NOH$

The neutral product (21) on treatment with HBr gave 2-ethylbenzo[b]furan-3-carboxylic acid[17]. The oxime (25) on rearrangement with dil. H_2SO_4 afforded 2-ethyl-3-hydroxy chromone, which was



The mixture of oximes (24) from the neutral product (14) was separated into two components having m.p. 156-57° and m p. 105° (one oxime reported earlier[8]). [Theoretically, each of the postulated diastereoisomers could afford two oximes (*syn* and *anti*) but only one is obtained in practice]. The pmr spectra[16] of both oximes are consistent with a chroman-3-one structure and in agreement with their diastereoisomeric relationship. The new oxime, m.p. 105°, on treatment with dil. $H_2SO_4^-$ also rearranged to give 2-methyl-3-hydroxychromone as was previously reported from the oxime, m.p. 156-57°. The yields of 2-methyl-3-hydroxychromone from each of the isomeric oxime were comparable. This transformation was explained in terms of Geissman structure as above (*cf.* Vargha[8]).

identical with that obtained from solvolysis of tosylate of (19).

In the solvolytic rearrangement[19] of tosylates of 2-substituted (and unsubstituted) benzofuryl-3-methyl ketoximes with aqueous methanol, only Beckmann rearrangement takes place. Further, the isomerisations of these *anti*-isomers to *syn*-forms with hydrogen chloride of 2-substituted (and unsubstituted) benzofuryl-3-alkyl ketoximes have been unsuccessful.

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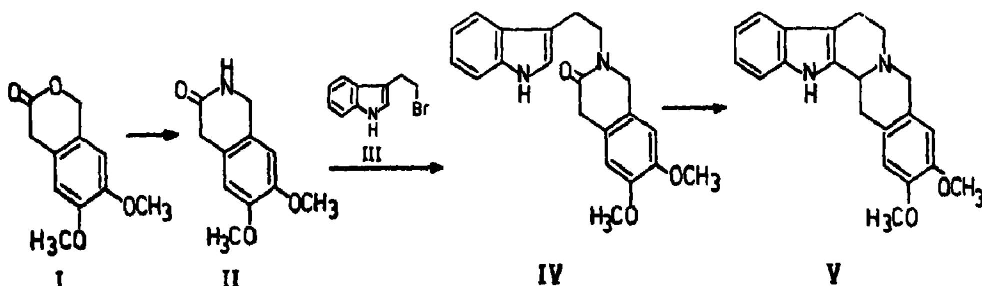
A Novel Synthesis of Yohimbane Skeleton[1]–Synthesis of 17,18-Dimethoxy-15,16,17,18,19,20-hexadehydroyohimbane by Condensation of an Indolylethylbromide with 3(2H)-isoquinolone

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Treatment of 6,7-dimethoxy-3-isochromanone with hydrazine followed by hydrochloric acid afforded 1,4-dihydro-6,7-dimethoxy-3(2H)-isoquinolone. Condensation of the isoquinolone with 2,3'-indolylethylbromide afforded the tetracyclic lactam which on phosphoryl chloride cyclization followed by sodium borohydride reduction gave the title compound in good yield, thereby providing an interesting entry to the yohimbane skeleton.

WE recently reported some convenient syntheses of the berbine alkaloids[2] employing the 3-isochromanones[3] and the bromo esters[4] derived from them. The 3-isochromanones has also been used successfully to synthesize the yohimbane alkaloids[5]. The most recent of the versatile uses of the 3-isochromanones made by us is the berbine synthesis being the condensation of the phenethyl bromide with 3(2H)-isoquinolone derived from 3-isochroma none. The present method of yohimbane synthesis essentially parallels the berbine synthesis[6], yet the significance of this method lies in the fact that it constitutes the first report of yohimbane alkaloid synthesis by this newly evolved reaction sequence. This method has the added advantage of placing the desired substitution on rings A and E of the yohimbane and also easy feasibility of the intermediates (Scheme 1).



Scheme 1

Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer 337 spectrophotometer and nmr spectra on a Wilmad (WCV 60) spectrometer using TMS as the internal standard. Solutions were dried over anhydrous sodium sulphate.

2-(2, 3'-Indolylethyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-3(2H)-isoquinolone (IV): To a solution of 2,3'-indolylethylbromide[7] (III) (225 mg) and 1,4-dihydro-6,7-dimethoxy-3(2H) - isoquinolone[6] (II) (195 mg) in absolute ethanol (12 ml) was added anhydrous K_2CO_3 (50 mg) and KI (10 mg). The mixture was refluxed under stirring at 100° for 32 hr, cooled, the solvent removed *in vacuo* and the residue diluted with excess water. The solution was extracted with $CHCl_3$ and the extract washed with water, dried and distilled. The residue crystallized from MeOH to give tetracyclic lactam (IV) as powder (160 mg, 50%), m.p. 74°; ir ($CHCl_3$), 1640 (six membered lactam), 3330 cm^{-1}. Found: C, 71.8; H, 5.9; N, 8.1. $C_{21}H_{21}N_2O_3$ requires C, 72.0; H, 6.28; M, 8.0%

17,18-Dimethoxy-15,16,17,18,19,20-hexadehydroyohimbane (V): Freshly distilled $POCl_3$ (2.0 ml) was added to a solution of the lactam (IV) (350 mg) in dry benzene (10 ml) and the solution was refluxed at 100° for 2.5 hr. The residue left after removal of the excess reagent and the solvent was treated with an excess of ice, the organic materials extracted in $CHCl_3$ and solvent removed *in vacuo* to leave a syrup. The syrup was dissolved in MeOH (7 ml) and treated with $NaBH_4$ (120mg) in portions during 30 min. After refluxing for 1 hr the solvent was removed, residue diluted with water and extracted with $CHCl_3$. Removal of the solvent and crystallization

from MeOH gave the compound (V) (155 mg, 47%), m.p. 250-51° (lit.[9], m.p. 249-50°); ir (KBr) 3335 cm^{-1}; nmr [$(CD_3)_2SO$] δ : 10.7 (broad, 1H, –NH), 7.5–6.8 (m, 4H, C–9H; C–10H; C–11H and C–12H), 6 75 (s, 2H, C–16H and C–19H), 4.2–4.0 (m, 1H, C–3H), 3.86 (broad, 2H, C–21H), 3.75 and 3.74 (2s, 6H, $-OCH_3$), 3 8–2 8 (m, 6H, C–5H, C–6H and C–14H) Found: C, 74.9; H, 6.2; N, 8.1. $C_{21}H_{22}N_2O_2$ requires C, 75.1; H, 6.5; N, 8.3%.

Acknowledgement

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Carbon-13 NMR Spectra of Angular and Linear Furanoflavones†

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^{13}C NMR spectra of four angular furanoflavones, lanceolatin B, karanjin, kanjone and 5-methoxyfurano(8,7-4″,5″)flavone and one linear furanoflavone, pinnatin were analysed and their carbon shifts assigned. Certain distinctive features of similarly substituted angular and linear furanoflavones have been pointed out.

THE occurrence of three new and eight known furanoflavonoids and five other flavonoids in the flowers of *Pongamia glabra* Vent. (Leguminosae) was recently reported by us[1,2]. To our knowledge, ^{13}C nmr spectral analysis of furanoflavonoids has not appeared in the literature till date. The present communication portrays the application of ^{13}C nmr spectroscopy to the major angular furanoflavones, lanceolatin B[1] (I), karanjin (II), kanjone (III), 5-methoxyfurano(8,7-4″,5″)-flavone (IV) and the only linear furanoflavone, pinnatin (V), occurring in the flowers of *P glabra*

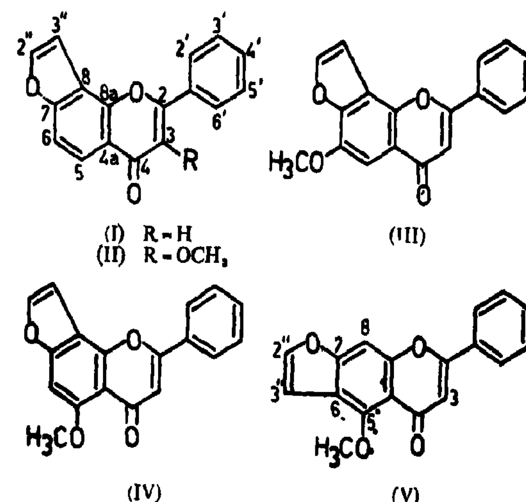
The assignments of the ^{13}C chemical shifts (δ_{TMS}, ppm) were based on the examination of the splitting pattern in the single frequency off-resonance decoupled spectra, comparison of the chemical shifts with the previously reported data for flavones[3-5] and furanocoumarins[6] together with the use of additive substituent parameters[7,8]. The assigned ^{13}C chemical shifts of the furanoflavones (I)—(V) are presented in Table 1. The salient features observed are discussed in the sequel

TABLE 1—^{13}C CHEMICAL SHIFTS (ppm) OF THE FURANOFLAVONES (I)—(V)

Carbons	(I)	(II)	(III)	(IV)	(V)
2	162.25	154 25	161 75	159 99	161 01
3	107.67	141 46	106.91	109 43	107 59
4	177 88	174 56	177.47	177.67	178 14
4a	119 14	119 29	119 62	110 02	112 58
5	121 49	121 41	99 64	157 97*	155.51
6	109.83	109 50	143 88	91 77	117 00
7	158.10	157 71	147.75	158.05*	157 83
8	116.94	116 60	116 50	111 03	95 19
8a	150 49	149.60	149 75	151 84	153 43
1′	131.35	130 61	131 39	131 15	131 34
2′	125 88	127 97	125 62	125 71	125 86
3′	128.90	128 29	128.65	128 34	128 76
4	131.35	130 31	130 98	131 15	131 14
5′	128 90	128 29	128 65	128 34	128 76
6′	125 88	127 97	125 62	125 71	125 86
2″	145.66	145.45	145 57	144 18	145.09
3″	103.96	103 84	104 22	103 82	105 18
OCH_3	—	59.80	56.00	56.62	61.60

* Assignments may be interchangeable

In the spectra of the angular furanoflavones (I)—(IV) the signal for C-8a having no *ortho* proton appeared as the least intense one around δ 150 while in the spectrum of the linear furanoflavone (V) the signal for C-4a (having no *ortho* proton) appearing at δ 112.58 and not C-8a was the least intense one. The deshielding of C-8a in (V) by 2-4 ppm relative to those in (I)—(IV) is noteworthy. The chemical shift for the carbonyl of flavones[4] (~178 ppm) remains almost unaffected by the fusion of the furano moiety to the flavone nucleus. The furan oxygen present on C-7 in the furanoflavones (I)—(V) shields C-4a (*para* position) by ~4 ppm whereas in simple flavones the shielding of C-4a by a 7-methoxy group[4] is ~6 ppm. It is worthwhile to mention



(I) R-H
(II) R-OCH_3
(III)
(IV)
(V)

here that in furanocoumarins[6] C-3 is shielded by ~4 ppm by the *para* orientation of the furan oxygen to the acrylic acid portion of the coumarin moiety. The chemical shifts of the carbons of the furano moiety (C-2″ and C-3″ here) are almost similar to those in furanocoumarins[6]. The chemical shifts of the methoxyls in 6-methoxy- angular furanoflavone (III) and 5-methoxy- angular furanoflavone (IV) are close to those observed[4] in cases of simple 6-methoxyflavone and 5-methoxyflavone respectively. In (III) the shielding effects of 6-methoxyl on the *ortho* carbons C-5 and C-7 are unequal (~22 and ~10 ppm respectively) and are similar to those observed[4] in case of 6-methoxyflavone. In (IV), the *ortho* carbon C-4a is shielded due to the 5-methoxyl by

†Dedicated, with profound regards, to Professor Nil Ratan Dhar, on the occasion of his 90th birthday in recognition of his contribution to chemistry and service to the nation.

~9.1 ppm, comparable to that observed[4] in case of 5-methoxyflavone. However, in (IV), the other *ortho* carbon C-6 is shielded by ~18 ppm and the *para* carbon C-8 by 5.9 ppm whereas the corresponding carbons in 5-methoxyflavone are shielded[4] by ~15 ppm and 11.7 ppm respectively. This difference in shielding effects between (IV) and 5-methoxyflavone may be ascribed to the fixation of the 7,8- double bond in (IV) due to the fusion of the furan moiety, thus reducing the electron relay from the methoxyl oxygen to C–8 and resulting in increased electron relay to C–6. In the case of karanjin (II) the signal of the 3-methoxyl appeared at somewhat lower field (~3 ppm) than those of the 5- and 6-methoxyls of (IV) and (III) respectively; further, this 3-methoxyl was found to exert shielding effects of ~3 ppm on the carbonyl shift and of 8 ppm on C–2 carbon shift.

Due to nonavailability of the unsubstituted linear furanoflavone, [furano (6,7-4″,5″) flavone], the expected ^{13}C nmr spectral difference between this linear furanoflavone and its angular isomer (I), arising out of the difference in the sites of the furan ring fusions only, could not be studied. Although the spectrum of the linear monomethoxyfuranoflavone (V) is available, the effect of the methoxy substitution on the linear furanoflavone molecule and its comparison with the same effect in the case of the angular furanoflavone could not be studied. However, some differences are observed when a comparison of the chemical shifts of the angular 5-methoxyfuranoflavone (IV) with those of its linear isomer (V) is made. Thus, C–6 in (IV) is more shielded (by ~3.5 ppm) than C–8 in (V). Again, the methoxyl signal in (V) appeared at a lower field (~5 ppm) than that in (IV); the greater deshielding in (V) may be due to the greater participation of its canonical form in which the aromaticity of the furan ring is restored than the canonical form of (IV) in which the furan aromaticity is lost[1]. Similar differences were observed in the ^{1}H nmr spectra of (IV) and (V)[1]. Furthermore, a diagnostic chemical shift difference of C–6 and C–8 in 5-methoxy angular and linear furanoflavones was also observed. Thus, C–6 of (V) resonated at a much lower field (~25 ppm) than that of (IV). Likewise, C–8 of (IV) also resonated at a significantly lower field (~16 ppm) than that of (V). Interestingly, the ring juncture carbon [C–6 in (V) and C–8 in (IV)] is more deshielded. This deshielding can presumably be attributed to the paramagnetic anisotropic effect of the furan ring on the ring juncture carbon. Moreover, the shielding effect of the 5-methoxyl is expected to be more pronounced at C-6 in (IV) as compared to that in (V) and at C-8 in (V) as compared to that in (IV) owing to the pronounced 7,8- double bond fixation in (IV) and the more electron relay from the methoxyl oxygen to C-8 restoring the aromaticity of the furan ring in (V).

Experimental

The furanoflavones (I)-(V) were obtained from the light petrol and chloroform extracts of the flowers of *P glabra*[1,2]: (I) m.p. 137°; (II), m.p. 161°, (III), m p 187-88°; (IV), m.p 176°, (V), m.p. 181°. The carbon-13 nmr spectra of all the compounds were taken in $CDCl_3$ at 0.25-0.50 molar concentrations with a Varian Associates CFT-20 (20 MHz) spectrometer. The chemical shift and degree of protonation of each carbon were determined by proton noise decoupling and single frequency off-resonance decoupling (SFORD) experiments respectively. The chemical shifts were taken from the computer generated print-out; the actual standard used was the centre line of $CDCl_3$ which was taken as 76.9 ppm downfield from TMS. Distinction of close resonance signals was done on the basis of qualitative relaxation characteristics.

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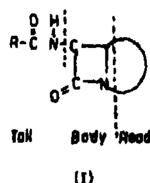
Synthesis of Some Novel β-lactam Derivatives

SITARAM SHARMA, J. K. RAY and BASANTA G. CHATTERJEE*

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One oxa-dethiacepham derivative containing one fused and one isolated β-lactam moieties has been synthesised utilizing the ketene-imine reaction and (2 + 2) cycloaddition of CSI to olefin. The synthesis of three novel tricyclic di-β-lactam derivatives is also reported. The bicyclic and tricyclic β-lactam derivatives have been characterised by ir and nmr spectral data and some by mass spectral data.

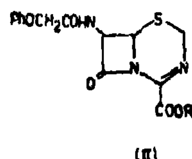
THE biological activity of the β-lactam antibiotic is generally believed to be associated with the chemical reactivity of their β-lactam ring which in turn is thought to be dependent on the tail end (amide side chain) as well as on the head of the antibiotic molecule[1].



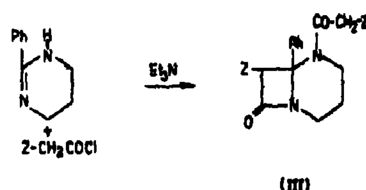
(I)

Initially, most of the research program was concerned with the modification of the tail end which lead to the introduction of a large number of clinically useful penam and cepham derivatives[2].

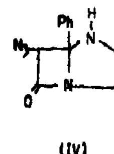
Subsequently, special attention was focussed on the modification of the head of the antibiotic molecule. Replacements of sulphur atom of these bicyclic compounds by carbon[3,4], nitrogen[5] or oxygen[6,7] were carried out in order to enhance the reactivity of azetidinone carbonyl function and consequently the antibacterial activity. Various ring homologues[8] have also been synthesised with similar objective A recent report[9] describes the synthesis of a novel biologically active compound (II) obtained by introducing a third hetero atom in place of C_3 of cephalosporin. More recently, some workers in this field got interested in the synthesis of compounds contaİning more than one β-lactam ring[10-15].


(II)

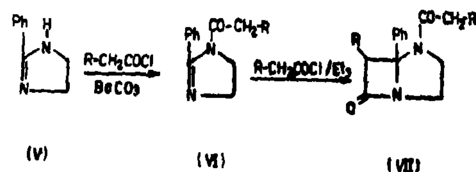
Prompted by the synthesis of novel aza-analogoue of cepham by Wolfe *et al*[16], Bose and coworkers[17] have recently communicated the total synthesis of some analogous compounds. They have successfully synthesised a number of 1-azadethiacepham derivative (III) by the 'acid chloride-imine' method.


(III)

However, their attempt to synthesise 1-azadethiapenam derivative (IV) from phenylimidazoline with azidoacetyl chloride in presence of triethylamine did not meet with desired success[17]. The failure of isolation of the penam analogoue in pure form was attributed to the striking decrease in stability in going from 1-azadethiacepham to the corresponding penam series.


(IV)

Since β-amino-β-lactams are unstable[18] because of participation of N-*p*-electrons in the ring opening reactions, we thought of synthesising the above penam analogue by blocking this participation through amidification of the imidazoline derivative.



(V) (VI) (VII)

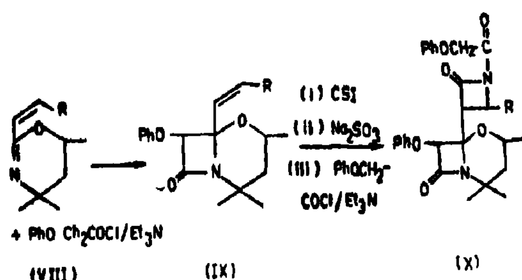
Reaction of 2-phenyl-imidazoline with phenoxyacetyl chloride in presence of barium carbonate gave amide (VI) in good yield. The product was characterised by ir and nmr spectral data. [IR ($CHCl_3$) : 1660 cm^{-1} (amide, carbonyl), 1620 cm^{-1} (imine function). NMR($CDCl_3$) δ : 3.6 (m, 4H), 4.45 (s, 2H), 6.9-7.8 (m, 10H) ppm].

The amide (VI) on reacting with further amount of phenoxyacetyl chloride in presence of triethylamine gave a semi solid mass, which resisted crystallization. The ir spectra not only affords an easy way of distinguishing between structure (V) and (VI)

but also between the structure (VI) and (VII). An open chain tertiary amide carbonyl group generally absorbs in the region 1650-1670 cm^{-1} [(VI)-1660 cm^{-1}]. In (VII) where the amide carbonyl group is part of a fused ring system, the ν C=O is shifted, as expected, to a much lower wave length (1785 cm^{-1}). The other peak, 1660 cm^{-1}, in the double bond region is attributed to the open chain amide carbonyl function. The assignment of the structure was further supported by the absence of a peak at 1620 cm^{-1} (C=N function).

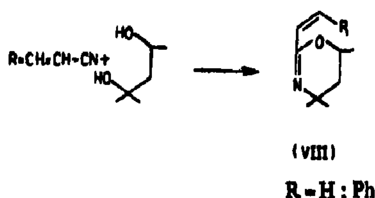
Attempts at purification of the compound, however, led to its decomposition to amide (VI) as characterised by m.m p. and ir spectra.

Since 1-aza- and 1-oxadethiacepham derivatives are readily obtainable from tetrahydropyrimidines[17] and dihydrooxazines[19] respectively, and since many of them are reported to be biologically active, it was thought of interest to synthesise a novel derivative (X) containing one more β-lactam ring. Our choice of preparing 1-oxadethiacepham was guided by the knowledge that replacement of sulphur atom at position 1 of the cepham nucleus with oxygen enhances the biological activity[20,21].



For building up the second β-lactam ring we utilized the cyclo-addition reaction between chlorosulphonyl isocyanate (CSI) and olefin (IX). The (2+2) cyclo-addition of CSI to olefins to produce β-lactams is a well documented reaction[22-24].

Oxazines (VIII) (2-alkenyl-4, 4, 6-trimethyl-5,6-dihydro-1,3-oxazine) were readily obtained from the reaction between commercially available 2-methyl-2, 4-pentandiol with unsaturated nitriles[25].

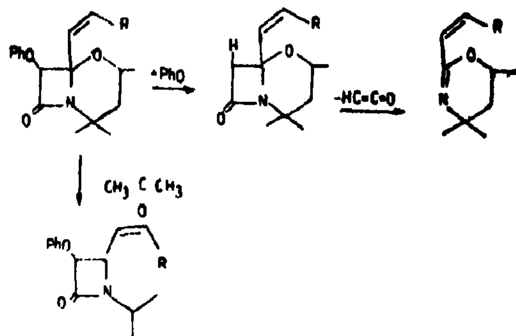


R = H ; Ph

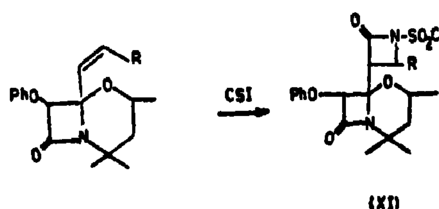
Compound	IR	NMR ($CDCl_3$) (δ) ppm	Mass spectra
IXa : R = Ph	1760 cm^{-1} (β-lactam)	1.35-1.8(m, 11H), 4.2(m, 1H), 5.0(s 1H); 6.2-6.5(m, 2H), 6.8-7.4(m, 10H)	363(M^+), 335, 295, 305, 229
IXb ; R = H	1760 cm^{-1} (β-lactam)	1.35-1.8(m, 11H) 4.2(m, 1H) 4.9(s, 1H) 5.2-6.2(m, 3H), 6.8-7.4(m, 5H)	287(M^+), 259, 229, 153

These derivatives, after usual characterisation, were reacted with phenoxyacetyl chloride in presence of triethylamine in methylene chloride solution at 0°. The isolated β-lactams, obtained in about 70% yield were characterised by ir, nmr and mass spectral data.

The mass fragmentation pattern is explained as under :



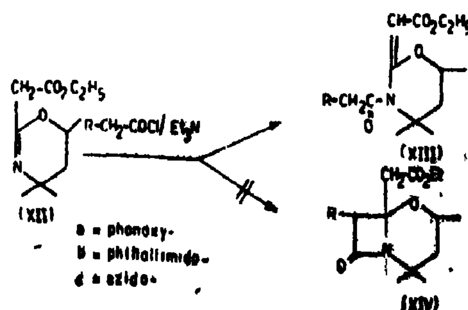
The reaction of CSI with the above fused β-lactam-oxazolidine derivative (IX) gave the N-chlorosulphonyl-β-lactam (XI).



Reductive hydrolysis followed by immediate amidification of the N-unsubstituted β-lactam gave the desired compound in 30-35% overall yield based on oxazine derivative (IX). The di-lactam (X) was a viscous semisolid mass giving a single spot on tlc and showed infrared absorptions at 1775 cm^{-1} (fused β-lactam carbonyl), 1750 (isolated β-lactam carbonyl) and 1685 cm^{-1} (amide carbonyl). The nmr spectrum is also in agreement with the assigned structure. NMR ($CDCl_3$) δ : 1.2-1.5(m, 11H), 4.2(m, 1H), 4.5-5.2(m, 5H), 6.8-8.4(m, 15H) ppm.

The reaction of CSI with (IXb), however, met with failure.

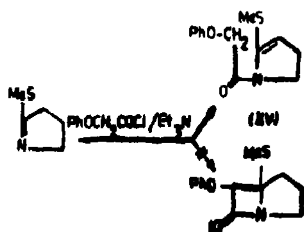
It is interesting to note here that the β-hydrogen atom of an imine often plays an important role in the 'ketene-imine' reaction. The oxazine derivative (XII) obtained from 2-methyl-2,4-pentandiol and cyanoacetic ester[26], on reaction with acid chloride-triethylamine gave the amide (XIII) rather than the β-lactam derivative (XIV).



The amides (XIII) were characterised by ir, nmr and mass spectral data. IR ($CHCl_3$): 1710 cm^{-1} (ester C=O), 1680 cm^{-1} (amide C=O).

The mass spectrum gives the molecular ion peak M^{+} 349 (for XIIIa). The singlet (2H) in nmr at 4.8 ppm is attributed to the phenoxymethylene proton. The other protons appear at their usual places. NMR ($CDCl_3$) δ : 1.1-1.8 (m, 14H), 4.1 (q, 2H), 4.4(m, 1H), 4.8(s, 2H), 6.7-7.2(m, 6H) ppm.

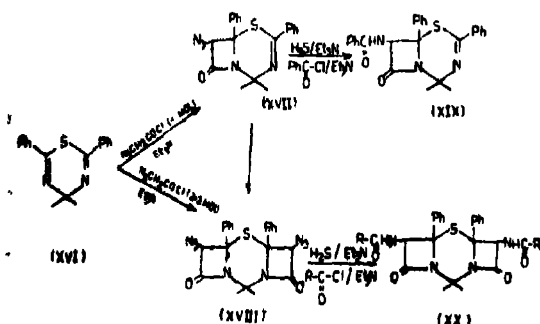
Bose *et al*[26] had also faced a similar practical problem in their attempt to synthesise exocyclic thio-analogue of penicillins and cephalosporins. The alkyl thio-group in the imine portion helped in the isomerisation of double bond resulting in the formation of unsaturated amide (XV).

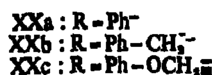


In an attempt to rectify the situation, we tried to react the imine (XII) with preformed phenoxyketene (reported stable)[27], to preclude isomerisation under basic condition. We were, however, unsuccessful in obtaining the phenoxy-ketene in pure form and the crude material failed to react with imine under the experimental conditions used.

The synthesis of some 3-azacephalosporins was first reported in 1980 by Mashimoto and coworkers[9]. The insignificant antibiotic activity of these compounds was attributed to the instability of the unsaturated molecule, for these compounds when reduced to 3-azacephams by Al/Hg in aqueous THF, were found to be biologically active.

The above observations coupled with easy access to thiadiazines, led us to synthesise some novel tricyclic-di-β-lactam derivatives.





2,6 - diphenyl - 4,4 - dimethyl - 4H - 1,3,5 - thiadiazine (XVI) was prepared by slightly modifying the method developed by Giordancdo and coworkers[28] involving condensation of thiabenzamide, acetone and benzonitrile in presence of borontrifluoroetherate. The yield of the product obtained by us was higher than the reported value.

When thiadiazine (XVI) was reacted with equimolar quantity of azido-acetyl chloride in methylene chloride at 0°, the azacepham [XVII : 2,2-dimethyl-4, 6-diphenyl- 7 -azido-8-oxo-5-thia-1,3-diazabicyclo-(4,2,0)-3-octene] was obtained as the major product (70% yield). The compound (XVIII) was also isolated from the reaction mixture as a minor product (15% yield).

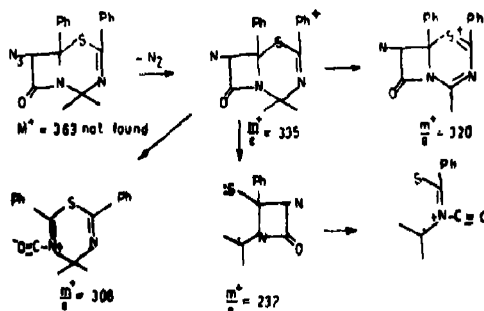
The structure of compound (XVII) was established by ir, nmr and mass spectral data as well as by elemental analysis.

The ir peaks at 2100, 1770, 1620 cm^{-1} are attributed to azido, β-lactam-carbonyl and imine functions respectively.

The nmr spectrum is also in agreement with the assigned structure. NMR ($CDCl_3$) δ : 1.3(s, 3H), 2.0(s, 3H), 5.0(s, 1H), 7.4(m, 8H), 7.9(m, 2H) ppm.

The gem dimethyl groups of thiadiazine (XVI) appear as a singlet (6H) at δ : 1.65 ppm. It is interesting to note that the gem dimethyl group of the product (XVII) appear as two singlets, one at δ : 1.3(3H) and the other at δ : 2.00(3H) because of the non-equivalence of gem dimethyl protons in the product.

Though the mass spectrum failed to show the molecular ion[29], the compound was well characterised by $(M-N_2)^+$ peak and the following fragmentation pattern.



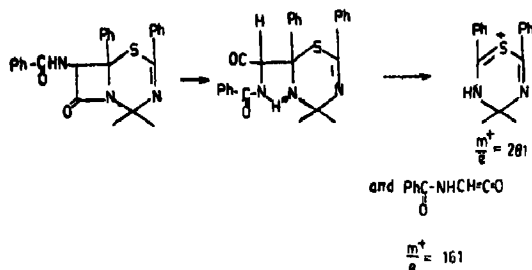
Our objective in using azido-acetyl chloride in above annelation reaction was to utilize the azido function to provide different amide chains at the desired position of the molecule. It has been established earlier that the β-lactam function is stable to the reagents needed to convert an azide to an amide *via* an amine. The products incidentally also helped in further characterisations of the cepham analogoues.

The conversion of an azido-derivative (XVII) to 7-benzamidocepham [XIX : 2,2-dimethyl-4, 6-diphenyl-7-benzamido-8-oxo-5-thia - 1, 3-diazabicyclo-(4,2,0)-3-octene] was carried out in the usual fashion[30,31]. Reduction with H_2S-Et_3N gave an amine which was coupled, without isolation, with benzoyl chloride-triethylamine to give the desired product in fairly good yield (65%).

The ir peaks at 3400, 1765, 1670 and 1620 cm^{-1} are attributed to N-H, β-lactam carbonyl, amide carbonyl and amine functions respectively.

The nmr spectrum shows the following pattern. NMR ($CDCl_3$) δ : 1.45(s, 3H), 2.00(s, 3H), 5.85(d, 1H), 7.0-8.0(m, 16H) ppm.

The mass spectrum gives the molecular ion peak at 441. Some of the fragments are explained as under :



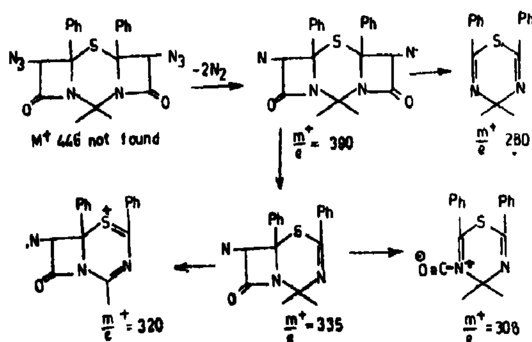
When thiadiazine (XVI) was treated with 2.2 moles of azido-acetyl chloride in presence of triethylamine, the compound [XVIII : 2,2-dimethyl-5,9-diazido-6,8-diphenyl-4,10-dioxo-1,3-diaza-7-thiatricyclo-(6,2,0,0^{3,6})-decane] was obtained in 65-70% yield.

The ir spectrum shows peaks at 2100, 1790 and 1770 cm^{-1} which are attributed to the azido and the two β-lactam carbonyl functions.

It is worthwhile to mention here that the gem dimethyl groups again appear as a singlet at δ : 2 0(6H) as a result of recreation of identical environment for the methyl protons in this molecule

The nmr spectra show the following pattern NMR ($CDCl_3$) δ : 2.00 (s, 6H) 4.4 (s, 2H), 7.5 (s, 10H) ppm

As is common to many azido-derivatives[29], this compound also does not show the molecular ion peak but gives $(M-56)^+$ peak[29]. The fragmentation pattern is explained as under :



The compound (XVII) was reduced with H_2S-Et_3N in methylene chloride to the diamino derivative which was amidified with three different acid chloride under basic conditions. The products (XXa, XXb, XXc) were characterised by ir and nmr spectra and elemental analysis.

Compound	IR spectrum	NMR ($CDCl_3$)δ ppm
XXa	3400, 1770, 1750, 1670 cm^{-1}	2,1(s, 6H), 5.4(m, 2H), 6.0(d, 2H), 7.2-7.7(m, 20H)
XXb	3370, 1770, 1750, 1680 cm^{-1}	1 9(s, 6H), 3 2(s, 4H) 5.1(d, 1H), 5.4(d, 1H) 6 7-7 5(m, 522H)
XXc	3370, 1770, 1755, 1690 cm^{-1}	2 1(s, 6H), 4.2(q, 4H)*, 5.3(d,2H) 6.5-7.6(m, 22H)

*The methylene protons (Ph-OCH_2) appears as a quartet. This type of non equivalence of methylene protons are known in the literature[33].

Experimental

All melting points are uncorrected. Pet. ether refers to the fraction b.p. 60-80°.

(a) *2,2,4-trimethyl-6-(β-styryl)-5-oxa-7-phenoxy-8-oxo-1-azabicyclo-(4,2,0)-octane* (IX) : A solution of VIII (2.3g ; 0.01 mole) and triethylamine (1.35 ml) in 40 ml dry methylene chloride was cooled to 0°. To this was added dropwise with stirring, phenoxyacetyl chloride (1.75 g ; 0 01 mole) in 15 ml methylene chloride and the stirring was continued overnight at room temperature. The mixture was washed with water, then with 10% aqueous $NaHCO_3$ solution and again with water. The organic layer was dried over Na_2SO_4. Removal of solvent afforded a solid residue, which was crystallized with pet. ether/methylene chloride to give white crystalline solid (2.8 g ; 70%) m p 132° IR($CHCl_3$) 1760 cm^{-1} (β-lactam C=O) ; nmr ($CDCl_3$)δ · 1 35-1 8 (m, 11H), 4 2 (m, 1H), 5 0 (s, 1H), 6.2-6.5 (m, 2H), 6.8-7.4 (m, 10H) ppm , MS - M^+ 363, 335, 305 etc. Found ; C, 75 85 ; H, 7 11 ; N, 3.62. Calcd. for $C_{22}H_{25}NO_3$, C, 76 00 ; H, 6 93 ; N, 3 85%.

(b) *2,2,4-trimethyl-6-(N'-phenoxyacetyl-2'-oxo-4'- phenyl- 3'-azetidinyl-)-5-oxa- 7-phenoxy- 8-oxo-1-azabicyclo-(4,2,0)-octane* (X) : To a solution of IXa (1.81 g ; 0 005 mole) in 50 ml dry methylene chloride was added dropwise with stirring CSI (0.71 g ; 0.005 mole) in 10 ml methylene chloride at −20°. The stirring was continued for 1 hr at −20°, and then another hr at 4°. The methylene chloride was removed under reduced pressure and the residue taken up in ether. The ethereal solution was added dropwise to a stirred mixture of Na_2SO_3 (10 ml, 25%) in ether (20 ml) maintained at 0°. The aqueous layer was made slightly alkaline by adding dilute potassium hydroxide solution. The organic layer was removed and the aqueous phase extracted with ether (20 ml x 3). The combined organic layer was dried over Na_2SO_4. The residue, obtained on removing the solvent, was redissolved in 10 ml dry methylene chloride, cooled to 0° and mixed with triethylamine (0.5 g). To this was added dropwise with stirring phenoxyacetyl chloride (0.85 g ; 0.005 mole) in 10 ml methylene chloride. The reaction mixture was stirred for 5 hr at room temperature. The mixture was washed with water, 10% aqueous sodium bicarbonate solution and again with water. The organic layer was dried over Na_2SO_4. The

solvent was removed and the residue was chromatographed over silica using pet. ether/methylene chloride (50 : 50) as eluent to yield a viscous semisolid mass (0.8 g ; 30%) giving single spot on tlc. IR ($CHCl_3$) : 1775 cm^{-1} (fused β-lactam C=O) 1750 cm^{-1} (monocyclic β-lactam C=O), 1685 cm^{-1} (amide C=O) ; nmr ($CDCl_3$) δ : 1.2-1.5 (m, 11H), 4.2 (m, 1H), 4.5-5.2 (m, 5H), 6 8-8.4 (m, 15H) ppm. Found : C, 71.32 ; H, 5.76 ; N, 5.32. Calcd. for $C_{32}H_{32}N_2O_6$; C, 71.09 ; H, 5.96 ; N, 5.18%.

(c) *2,2 - dimethyl-4,6-diphenyl-7-azido-8 - oxo-5-thia-1,3-diazabicyclo-(4,2,0)-3-octene* (XVII) : A solution of thiadiazine (XVI) (2.8 g ; 0.01 mole) and triethylamine (1.35 ml) in 60 ml dry methylene chloride was cooled to 0°. To this was added, with stirring over a period of 30 min, a solution of azidoacetyl chloride (1.2 g ; 0.01 mole) in 20 ml of methylene chloride. The mixture was stirred for 1 hr at 0° and then 2 hr at room temperature. The reaction mixture was thoroughly washed with water. The organic layer was dried over Na_2SO_4. Removal of solvent afforded a brown residue which when chromatographed over silica using ether/methylene chloride (40 : 60) as eluent gave first a solid crystalline material (XVII) (2.5 g ; 70%, m.p. 119°) and then XVIII (0.5 g ; 15%, m.p. 160° decomp.). IR (XVII) ($CDCl_3$) : 2100 cm^{-1} (azido), 1770 cm^{-1} (β-lactam C=0), 1620 cm^{-1} (—C=N) ; nmr ($CDCl_3$) δ : 1.3 (s, 3H), 2.0 (s, 3H), 5.0 (s, 1H), 7.4 (m, 8H), 7.9 (m, 2H) ppm ; MS 335 (M^+—28) 320, 308. Found : C, 62.93 ; H, 4. 87 ; N, 19.45. Calcd. for $C_{19}H_{17}N_5OS$; C, 62.79 ; H, 4.71 ; N, 19.27%.

(d) *2,2-dimethyl-4,6-diphenyl-7-benzamido-8-oxo-5 - thia - 1,3-diazabicyclo - (4,2,0) - 3 - octene* (XIX) : H_2S was bubbled into a solution of XVII (1.1 g ; 0.003 mole) in 40 ml methylene chloride containing triethylamine (0.6 ml) for 10 min at 0°. After stirring 1 hr the solvent was removed under reduced pressure and the residue sucked dry under high vaccum.

The crude amine was redissolved in 30 ml dry methylene chloride and cooled to 0° and was mixed with triethylamine (0.5 ml). To this was added dropwise with stirring, benzoyl chloride (0 450 g) in 10 ml methylene chloride. The reaction mixture was stirred for 5 hr at room temperature. It was then washed with water, 10% aqueous $NaHCO_3$ solution and finally with water. The organic layer was dried over Na_2SO_4. Removal of solvent and crystallisation of the residue with pet. ether/methylene chloride gave white crystalline material (0.8 g ; 65%, m.p. 181°). IR ($CHCl_3$) : 3400 cm^{-1} (N—H), 1765 cm^{-1} (β-lactam C=O), 1670 cm^{-1} (amide C=O), 1620 cm^{-1} (C=N) ; nmr ($CDCl_3$) δ : 1.45 (s, 3H), 2.00 (s, 3H), 5.85 (d, 1H), 7.0-8.0(m, 16H) ppm ; MS 441, 281, 161. Found : C, 70.57 ; H, 5.34 ; N, 9.33. Calcd. for $C_{26}H_{23}N_3O_2S$; C, 70.72 ; H, 5.25 ; N, 9.52%.

(e) *2,2-dimethyl - 6,8-diphenyl-5,9-diazido-4,10 - dioxo-1,3 - diaza-7-thiatricyclo - (6,2,0,0^{3,6}) decane* (XVIII) : The compound was obtained on treatment of thiadiazine (2.8 g) with 2.2 molar ratio of the azido-acetyl chloride and working up as before (see experiment-c). Yield (3.1 g ; 65%, m.p. 160° decomp). IR ($CHCl_3$) : 2100 cm^{-1} (azido), 1790 cm^{-1}, 1770 cm^{-1} (β-lactam C=O) ; nmr ($CDCl_3$) δ : 2 0 (s, 6H), 4.4 (s, 2H), 7.3 (m, 10H) ppm. MS 390 (M^+—56), 335, 320, 280 etc. Found : C, 56.31 ; H, 4.13 ; N, 25.17. Calcd. for $C_{21}H_{18}N_8O_2S$; C, 56.49 ; H, 4.06 ; N, 25.09%.

(g) *2,2 - dimethyl-6,8-diphenyl-5,9-diphenylacetamido - 4,8 - dioxo-1,3-diaza-7-thiatricyclo-(6,2,0,0^{3,6})-decane* (XXb) : Yield 70%, m.p. 212° (decomp). IR ($CHCl_3$) : 3370 cm^{-1} (N—H), 1770, 1750 cm^{-1} (β-lactam C=O), 1685 cm^{-1} (amide C=O) ; nmr ($CDCl_3$) δ : 1.9(s, 6H), 3.2(s, 4H), 5.1(d, 1H), 5.4 (d, 1H), 6 7—7.5(m, 22H) ppm. Found : C, 70.18 ; H, 5.52 ; N, 8.76 Calcd. for $C_{37}H_{34}N_4O_4S$; C, 70.45 ; H, 5.35 ; N, 8 83%.

(h) *2, 2-dimethyl-6,8-diphenyl-5,9-diphenoxyacetamido-4,8-dioxo-7-thia-1,3 - diazatricyclo-(6,2,0,0^{3,6})-decane* (XXc) : Yield 70%, m.p. 196° (decomp). IR ($CHCl_3$) : 3370 cm^{-1} (N—H), 1770 cm^{-1}—1755 cm^{-1} (β-lactam C=O), 1690 (amide C=O) ; nmr ($CDCl_3$) δ : 2.1 (s, 6H), 4.2 (q, 4H), 5.3 (d, 2H), 6.5-7.6 (m, 22H) ppm. Found C, 66.97 ; H, 5.02 ; N, 8.49. Calcd. for $C_{37}H_{34}N_4O_6S$; C, 67.05 H, 5.17 ; N, 8.45%.

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3,4-Bond Cleavage of Tetrahydro-β-Carboline Alkaloids : Transformation of Venenatine and Rhazine to the Corresponding 2-Acylindole Derivatives

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3,4-Bond cleavage reactions of venenatine (1) and rhazine (6) with cyanogen bromide in ethanolic chloroform were studied The resulting seco-bases were transformed to the corresponding 2-acylindoles with *t*-BuOCl

MANY 2-acylindole alkaloids are known to co-occur with tetrahydro-β-carboline bases in plants[1,2]. Hence it is reasonable to suppose that these 2-acylindoles are biogenetically derived from the corresponding tetrahydro-β-carboline bases by a reaction sequence the key step of which involves a 3,4-bond cleavage with subsequent oxidation at C-3. Though definite evidence involving *in vivo* experiments with radio-labelled compounds is lacking, laboratory analgoies[3-8] for this transformation are known. We have been interested for some time in this type of transformation[6] and in the present paper we report the results of our studies on the 3,4-bond cleavage reaction of venenatine[9] (1), an yohimbinoid alkaloid of *Alstonia venenata*, and rhazine[10,11] (6), a sarpagine-type base of *Rhazya stricta*, with the intension of converting these to the corresponding 2-acylindoles.

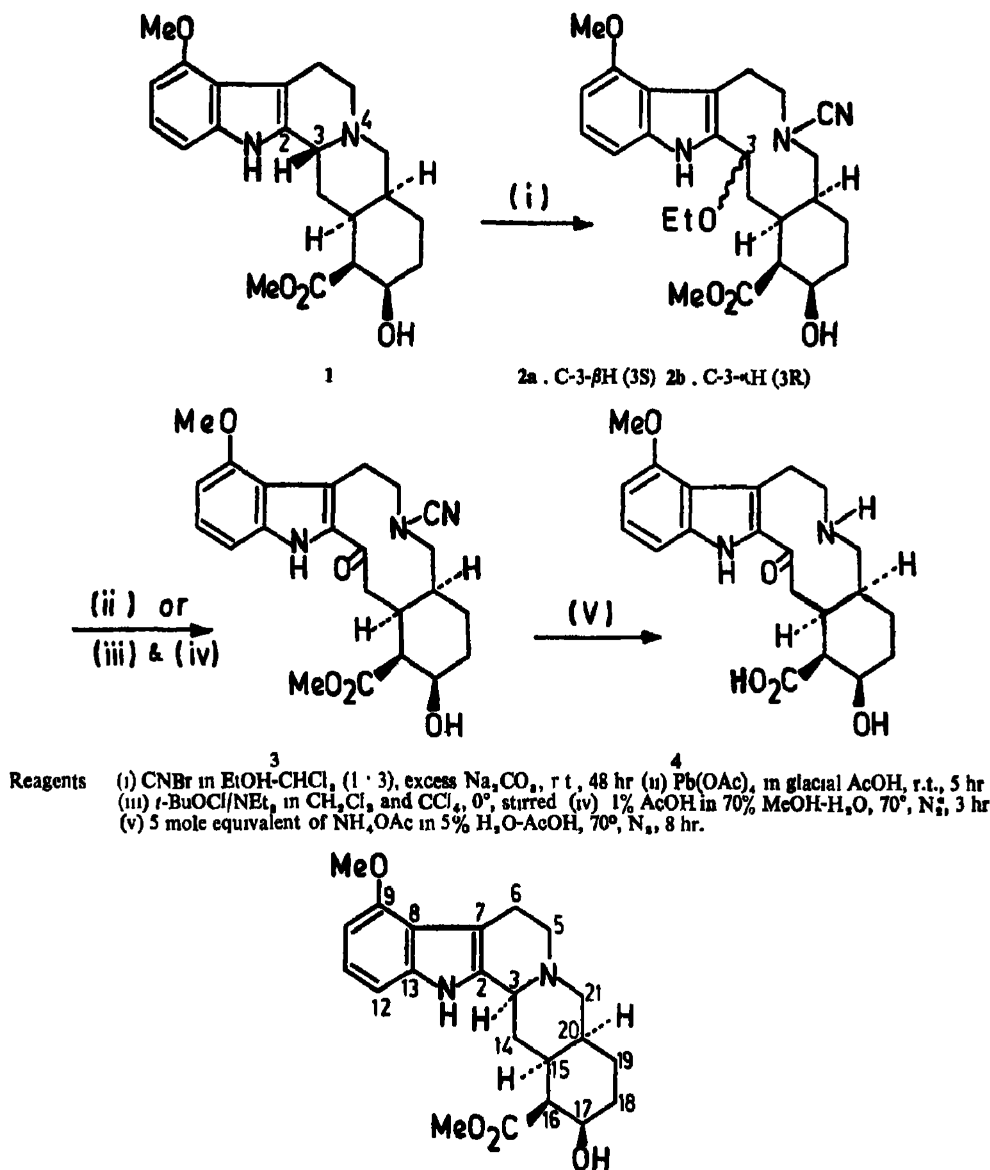
Results and Discussion

Transformation of venenatine (1) : Venenatine (1) was converted to its 2-acylindole derivative in three steps as shown in Scheme I The 3,4-bond cleavage in venenatine was brought about by treatment with CNBr in EtOH-$CHCl_3$ in the first step, when two products (**2a** and **2b**) were obtained The structures of **2a** and **2b** were settled on the basis of detailed spectroscopic studies and chemical reactions. The mass spectra of these compounds exhibited molecular ion peaks at m/e 455 corresponding to the molecular formula $C_{25}H_{33}N_3O_5$, having additional $-CN$ and $-OCH_2CH_3$ groups to venenatine. In addition to the MS, the other spectral data (uv, ir, ^{1}H- and ^{13}C-nmr) of **2a** and **2b** confirmed their structures to be 3-ethoxy-3,4-secocyanamide of venenatine (1). The ^{1}H-nmr spectra of **2a** and **2b** showed the presence of ethoxy protons and the expected shift of the C-3-*H* to δ4.66 and δ4.10 respectively, from that of venenatine (at δ4.45)[9]. The stereochemisty at C-3 was settled on the basis of stereospecific ring closure reactions of **2a** and **2b** with glacial acetic acid at 70° to venenatine (1) and alstovenine (5) respectively[9]. Both ring closures furnished exclusively one product. The ring closures occurred by an acid-catalysed direct S_N2 displacement of the ethoxy groups. Hence it was confirmed that **2a** was 3S and **2b** the 3R-compound Sakai *et al*[9] had earlier made similar stereochemical assignments for the 3-ethoxy-3,4-secocyanamides of yohimbine and hirsutine.

The 20 MHz ^{13}C-nmr spectra of **2a** and **2b** were studied in $CDCl_3$. The assignment of the ^{13}C-shifts of these compounds have been made on the basis of the comparison of the δ values with those of venenatine[11] and also on the basis of SFORD multiplicities. The assignments are shown in Scheme II Characteristic new signals were discernible for the cyano and the ethoxy carbons in the spectra of **2a** and **2b** Moreover, the C-3 showed the expected downfield shift of *ca* 20 ppm in the seco-products with respect to that of venenatine (venenatine C-3 appears at 53.8 ppm)[11]. The chemical shifts of this carbon, however, differed by 3.7 ppm for the diastereoisomeric **2a** and **2b**. An interesting observation was that C-12 had shifted upfield by *ca* 6 ppm in the seco products in comparison with that of venenatine (venenatine C-12 appears at 105.7 ppm)[11].

The next step (Scheme I) was the formation of the 3-keto-3,4-seco-cyanamide derivative (3) from the 3-ethoxy derivatives, **2a** and **2b**. A mixture of **2a** and **2b** was treated with $Pb(OAc)_4$ in glacial AcOH at room temperature to give a complex mixture of products from which 3 was isolated in low yield by preparative tlc. However, the yield could be dramatically improved when the oxidation was carried out with *t*-BuOCl. In this case 3 was obtained in 85% yield on subsequent warming with water in presence of traces of acid. The uv spectrum of 3 exhibited absorption maxima [311, 249 and 206 nm (log ε : 2.93, 3.08 and 3.26)] characteristic of 2-acylindoles, the presence of which moiety was further substantiated by the appearance of an ir band at 1710 cm^{-1} (α,β-unsaturated >C=O). The absence of ethoxy protons and the C-3-*H* in ^{1}H-nmr spectrum and the absence of the ethoxy carbons and appearance of a downfield signal (at 193.1 ppm,

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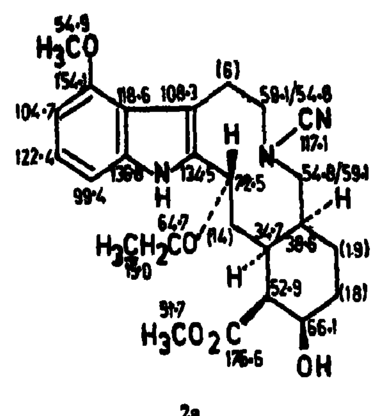
Reagents (i) CNBr in EtOH-$CHCl_3$ (1 · 3), excess Na_2CO_3, r t, 48 hr (ii) $Pb(OAc)_4$ in glacial AcOH, r.t., 5 hr (iii) t-BuOCl/NEt_3 in CH_2Cl_2 and CCl_4, 0°, stirred (iv) 1% AcOH in 70% MeOH-H_2O, 70°, N_2, 3 hr (v) 5 mole equivalent of NH_4OAc in 5% H_2O-AcOH, 70°, N_2, 8 hr.

Scheme I. Conversion of 1 to 4

assigned to C-3 carbonyl) in the ^{13}C-nmr spectrum also confirmed the structural assignment as 3.

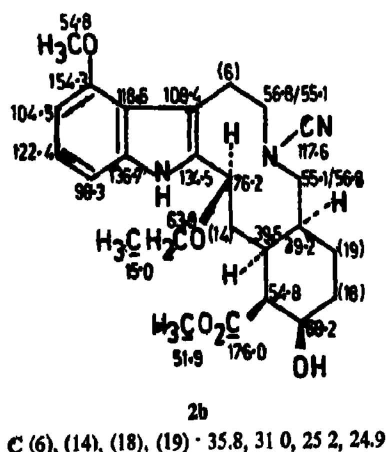
In the final step, conversion of 3 to 4 (Scheme I) was achieved by treating the former with 5 mole equivalent of NH_4OAc in glacial AcOH 4, $C_{21}H_{26}N_2O_5$ (M^+ 386). was obtained in rather poor yield (*ca* 10%). The N-decyanation was accompanied by hydrolysis of the ester group As this process of conversion of N-CN to N-H, originally adopted by Sakai *et al*[8], was not very satisfactory, we attempted to effect the same conversion by passing HCl gas into a methanolic solution of the alkaloid and subsequent hydrolysis. However, this did not result in any significant improvement of the yield. The ir spectrum (KBr) of the product 4 showed the absence of any band around 2200 cm^{-1} (for —CN), but a broad hydroxyl band appeared at 3400-3200 cm^{-1}.

Transformation of rhazine (6) : Conversion of rhazine (6) into its 2-acyl derivative (7) was achieved in two steps (Scheme III). Due to paucity of the material, further studies in this series could not be made Rhazine (6) was treated with cyanogen bromide under the same conditions employed in case of venenatine (Scheme I). Two products (6a and 6b) were isolated and their structures were settled to be 3-ethoxy-3,4-seco-cyanamide derivative of rhazine, on the basis of detailed spectroscopic studies (uv, ir, MS, ^{1}H- and ^{13}C-nmr). The stereochemistry at C-3 could not be determined by stereospecific ring closure reaction with glacial acetic acid as in the case of venenatine, since the reaction with



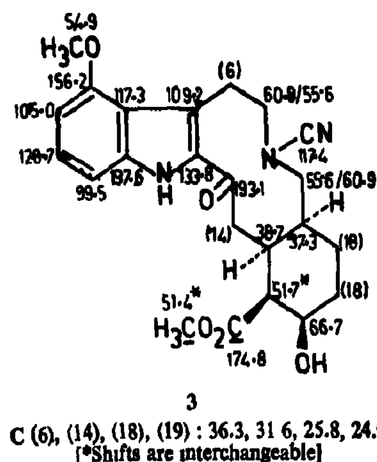
2a

C (6), (14), (18), (19) . 39 6, 30.2, 26 2, 24 3



2b

C (6), (14), (18), (19) · 35.8, 31 0, 25 2, 24.9



3

C (6), (14), (18), (19) : 36.3, 31 6, 25.8, 24.9

[*Shifts are interchangeable]

Scheme II. ^{13}C-shift (in ppm) assignment of **2a**, **2b** and **3**.

glacial acetic acid led to a complex mixture of products which included unreacted starting materials in large amount. A tentative suggestion regarding the stereochemistry has been made from analogy. Venenatine (**1**) under the same solvolytic conditions of the cleavage reaction afforded predominantly the C-3 inversion product. Hence, it may be suggested that **6a**, the major product, was the "3R" compound, as the starting material, rhazine (**6**), has a "3S" configuration. Since **6a** and **6b** are epimeric at C-3, **6b** would therefore presumably be the 3S compound.

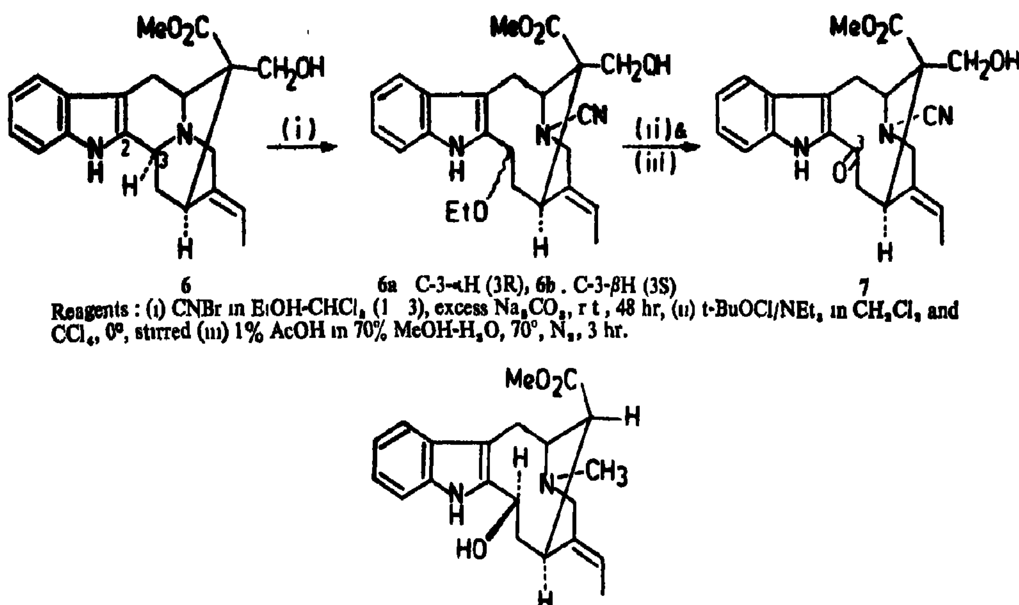
The 20 MHz ^{13}C-nmr spectra of **6a** and **6b** were studied in $CDCl_3$. These were in agreement with the proposed seco-structures. The assignments of the carbon signals of these compounds have been made on the basis of comparison of the chemical shifts of vobasinol[13] (**8**), multiplicities of the signals in the SFORD spectra and intercomparisons (Scheme IV). The C-3 carbon showed a downfield shift of *ca* 6.2 ppm in the seco-products (**6a** and **6b**) with respect to that of vobasinol (**8**)[13] (vobasinol C-3 appears at 66.8 ppm) presumably due to the α-effect caused by the O-alkyl substituent.

In the next step (Scheme III) the seco products (**6a** and **6b**) were converted to 3-keto-3,4-secocyanamide derivative (**7**) by treatment with *t*-BuOCl. **7** exhibited uv absorption maxima typical of 2-acylindole. It showed the absence of C-3-*H* and the ethoxy protons in the ^{1}H-nmr spectrum and the appearance of an ir band at 1705 cm^{-1} for α,β-unsaturated carbonyl in addition to the other expected bands. All these data point to the 3-keto-3,4-seco-cyanamide structure for **7**. One point needs mention in this connection is that in the ^{1}H-nmr the ester methyl resonated at δ 3.73 instead of resonating at *ca* δ 2.50, a characteristic value for the sarpagine-type alkaloids and the corresponding 3-ethoxy-3,4-seco derivatives. This indicated a conformational change of the 10-membered ring (previously rings C and D), so that the carbomethoxyl group was no longer situated in the shielding region of the aromatic nucleus.

Experimental

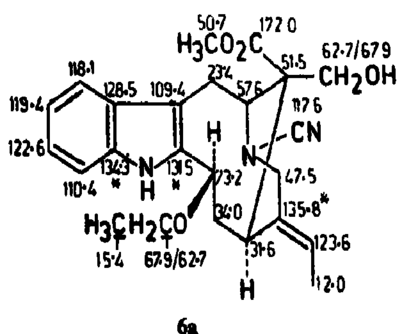
Melting points were recorded on an electrically heated Kofler Block and are uncorrected. The uv spectra were recorded on a Varian 634S spectrophotometer in 95% aldehyde-free ethanol. The ir spectra were recorded in KBr disc on a Beckman IR-20 spectrophotometer and the rotations measured on a Perkin-Elmer 241 polarimeter. The ^{1}H- and ^{13}C-nmr spectra were recorded on Varian CFT-20 NMR spectrometer in $CDCl_3$ using TMS as internal standard. Brockman alumina (basic) (B.D.H.) was used for column chromatography; silica gel G (Gouri Chemicals, Calcutta) and alumina G(B.D.H.) were used for thin layer chromatography. Reactions were carried out with authentic samples of rhazine and venenatine isolated earlier in our laboratory.

Preparation of **2a** *and* **2b**: CNBr (424 mg; 4 mmole) was added with stirring to a solution of venenatine (**1**) (382 mg; 1 mmole) in dry EtOH-$CHCl_3$ (1 : 3) (100 ml). Anhydrous Na_2CO_3 (1.0 g) was added and the reaction mixture kept for 48 hr at room temperature. It was then filtered and the filtrate was concentrated under reduced pressure. The two products **2a** (R_f 0.50) and **2b** (R_f 0.60), were isolated by ptlc on alumina chromatoplates using EtOAc as the developing solvent. Overall isolated yield of the seco-products was 85% (**2a**, 60%; **2b**, 25%). **2a** (275 mg; 60%) was isolated as an yellow solid, $C_{25}H_{33}N_3O_5$, m.p. 204-205°, $[\alpha]_D$ -131·6° (EtOH). Found: C, 65.78; H, 7.42; N, 9.08. $C_{25}H_{33}N_3O_5$ requires C, 65.91; H, 7.30; N,

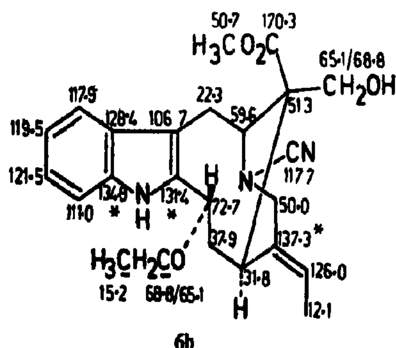


8 · Vobasinol

Scheme III Conversion of 6 to 7



6a



6b

[*Shifts are interchangeable]

Scheme IV. ^{13}C-shift (in ppm) assignment of 6a and 6b.

9.22%. MS [m/e (relative abundance %)] : 455(M^+, 20), 420 (15), 409 (10), 281 (18), 230 (10), 209 (18), 208 (20), 207(100), 191(15) 145(18), 133(10), 117(10). IR ν_{max} cm^{-1} : 3400(-OH, -NH) ; 2230 (-C≡N) ; 1730 (ester >C=O) ; 1165, 1125, 1100 (—C—O— stretching) ; 1100, 1070, 780, 740 (1,2,3-tri-substituted phenyl nucleus). UV (EtOH) λ_{max} ; 235, 270, 282 (sh) and 292 nm (log ε : 4.57, 3.93, 3.81 and 3.76). 80 MHz ^{1}H-nmr ($CDCl_3$) δ : 1.15 (3H, t, J=7.0 Hz ; -OCH_2CH_3) ; 3.30(2H, q, J=7.0 Hz ; -OCH_2CH_3) ; 3.70 and 3.79 (3H, s each ; -CO_2CH_3 and 9-OCH_3) ; 3.91 (1H, m ; C-17-H) ; 4.66 (1H, d of d with fine splitting, J_1=6.0 Hz, J_2=3.5 Hz ; C-3-H) ; 6.38 (1H, d of d, J_o=6.0 Hz, J_m=2.9 Hz ; C-10-H) ; 6.91-6.98(2H, m; C-11-H and C-12-H) ; 8.43 (1H, br s, disappeared on deuteration ; indole -N-H).

2b (114 mg ; 25%) was isolated as an yellowish solid, $C_{25}H_{33}N_3O_5$, m.p 123-25°, $[\alpha]_D$-30.7°(EtOH). Found : C, 65.82 ; H, 7.19, N, 9.41. $C_{25}H_{33}N_3O_5$ requires C, 65.91: H, 7.30. N, 9.22%. MS [m/e(%)] : 455(M^+, 100), 426(50), 410(25), 409(30), 382(10), 230(10), 229(9), 200(5), 199(10), 188(20), 160(15), 130(5). IR ν_{max} cm^{-1} : 3400(-OH and/or -NH-) ; 2220 (-C≡N) ; 1730 (ester >C=O) ; 1160, 1140, 1110 (—C—O—stretching), 1110, 1090, 980, 780, 735 (1,2,3-trisubstituted phenyl nucleus). UV (EtOH) λ_{max} : 225, 270, 281sh, 293 nm (log ε : 4.59, 3.90, 3.82 and 3.78). 80 MHz ^{1}H-nmr ($CDCl_3$) δ : 1.05 (3H, t, J=6.9 Hz, -OCH_2-CH_3) ; 3.22 (2H, q, J=6.9 Hz ; -OCH_2-CH_3) ; 3.74 and 3.80 (3H, s each ; -CO_2CH_3 and 9-OCH_3) ; 3.98 (1H, m ; C-17-H) ; 4.10 (1H, d of d with fine splitting, J_1=6.0 Hz, J_2=3.5 Hz ; C-3-H) ; 6.38 (1H, d of d, J_o=6.7 Hz, J_m=1.5 Hz ; C-10-H) ; 6.98-6.87 (2H, m ; C-11-H and C-12-H) ; 8.17 (1H, br s, disappeared on deuteration ; indole -NH-).

Ring closure reactions of **2a** *and* **2b** : **2a** (5 mg) was warmed in glacial acetic acid (1 ml) at 70° under nitrogen atmosphere for 3 hr. The reaction mixture was then poured into 10 ml of water, cooled (0°), made alkaline with ammonia and extracted with $CHCl_3$ (20 ml×3). The $CHCl_3$ extract was

washed with water, dried (Na_2SO_4), and concentrated to give venenatine (1) (identified by m.m.p., co-tlc and superimposable ir with authentic sample), m.p. 123-26° (dec); yield 4.5 mg (100%). TLC of the $CHCl_3$ extract showed the absence of any alstovenine (5).

The ring closure reaction of **2b** was carried out employing the above reaction conditions and work-up procedure. This reaction afforded a quantitative yield of alstovenine (5) (identified by m m.p, co-tlc and superimposable ir with authentic sample). The reaction mixture showed the absence of any venenatine (1) on tlc

Preparation of 3 . *Pb(OAc)₄ method*: $Pb(OAc)_4$ (49 mg, 0 11 mmole) was added to a solution of **2a** and **2b** (50 mg; 0.11 mmole) (crude reaction mixture obtained in first step without separation). The mixture was stirred at room temperature for 10 hr and filtered The filtrate was diluted with water (20 ml), made alkaline with ammonia at 0° and then extracted with CH_2Cl_2 (50 ml × 4); the CH_2Cl_2 extract was dried (Na_2SO_4) and concentrated The 3-keto-3,4-seco-cyanamide derivative (3) was isolated in very low yield (*ca* 5 mg; *ca* 10%) by ptlc of the concentrate on silica gel plates using 10% MeOH-EtOAc as the solvent system.

t-*BuOCl method*. A mixture of **2a** and **2b** (455 mg, 1 mmole) dissolved in 25 ml of CH_2Cl_2 was kept at 0° in an ice-salt bath. An equimolar amount of *t*-BuOCl (110 mg; 1 mmole) in 25 ml of CCl_4 was added to the reaction mixture over a period of 1 hr with stirring. After addition was complete the solution was stirred for 30 min with no external cooling. The yellow solution was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure to give a viscous deep brown mass This mass was dissolved in 1% glacial AcOH in 70% $MeOH-H_2O$, heated at refluxing temperature under nitrogen atmosphere for 3 hr. The methanol was removed from the reaction mixture under reduced pressure and the product was isolated following the usual procedure The crude product on chromatography over alumina yielded 3 from the C_6H_6-EtOAc (1 : 1) eluates in colourless needles, $C_{23}H_{27}N_3O_5$, m p, 260-62°(dec) (yield 361 mg; 85%), $[\alpha]_D + 261\ 2°$ (EtOH) Found: C, 64.73; H, 6.54; N, 9.72. $C_{23}H_{27}N_3O_5$ requires C, 64.93; H, 6.40; N, 9 88%. MS [m/e (%)]: 425 (M^+, 100), 406(15), 397(18), 396(18), 382(10), 213(15), 207(22), 202(15), 200(10), 199(15), 198(10), 188(10), 187(10), 186(15), 174(40), 173(95), 172(15), 160(30), 144(15) 130(25), 77(10). IR ν_{max} cm^{-1}: 3480, 3340 (-NH- and -OH); 2220 (-C≡N), 1730 (ester >C=O); 1710 (α,β-unsaturated >C=O); 1115, 990, 790, 745 (1,2,3-trisubstituted phenyl nucleus). UV (EtOH) λ_{max}: 311, 249 and 206 nm (log ϵ: 2.93, 3.08 and 3 26). 80 MHz ^{1}H-nmr ($CDCl_3$) δ: 3.69 and 3.81 (3H, s each; 9-OCH_3 and -CO_2CH_3); 4.11 (1H, m; C-17-*H*); 6.33 (1H, d of d, J_o=6.7 Hz, J_m=1.2 Hz; C-10-*H*); 6.83 (1H, d of d, J_o= 7.7 Hz, J_m=1.2 Hz; C-12-*H*); 7.04 (1H, d, J=7. Hz; C-11-*H*); 9.03 (1H, br s, disappeared o deuteration; indole -N*H*-).

Preparation of 4: Compound 3 (100 mg; 0.2 mmole) was dissolved in 5% H_2O-AcOH (25 ml) Ammonium acetate (85 mg; 1.10 mmole) was adde and the reaction mixture was heated at 70° unde nitrogen atmosphere for 8 hr. After the usua work-up the product on chromatography ove alumina column yielded the decyano derivative, 4 from the EtOAc-MeOH (9 : 1) eluates as a amorphous powder, $C_{21}H_{26}N_2O_5$, (yield: 10 mg 10%). Found: C, 65.04; H, 6.91; N, 7.15 $C_{21}H_{26}N_2O_5$ requires C, 65.27; H, 6.78; N, 7.25% MS [m/e (%)]: 386 (M^+, 5), 385(25), 384(100) 383(75), 382(60), 381(10), 380(8), 378(5), 372(5) 360(8), 353(5), 324(5), 323(10), 318(8), 252(5) 251(8), 250(5), 216(12), 214(12), 198(5), 105(8 IR ν_{max} cm^{-1}: 3400-3200 (-NH- and -OH); 173 (acid >C=O); 1700 (α,β-unsaturated >C=O) 1170, 1155, 1110, 790 and 750 (1,2,3-trisubstitute phenyl nucleus).

Preparation of **6a** *and* **6b**: Rhazine (6) (176 mg 0.5 mmole) was treated with cyanogen bromid (212 mg, 2 mmole) under identical condition employed for the preparation of **2a** and **2b**, usin the same molar proportions. A similar work-up o the reaction mixture gave **6a** (R_f 0.44) and **6b** (R 0 48), which were separated by preparative tlc o silica gel chromatoplates using benzene : ethylacetat (1 : 1) as the developing system. Overall isolate yield 85% (**6a** 115 mg, 55%; **6b** 64 mg, 30%) 6 was isolated as an yellow powder, $C_{24}H_{29}N_3O_4$ m p 128-131° $[\alpha]_D + 30.1°$ (EtOH). Found: C, 68.21 H, 7 06, N, 9 78. $C_{24}H_{29}N_3O_4$ requires C, 68.07 H, 6 90; N, 9 92%. MS [m/e (%)]: 423 (M^+, 50 393(10), 377(5), 364(5), 318(10), 205(15), 200(20 193(15), 191(30), 188(10), 174(50), 157(20), 156(100 133(5), 130(60). IR ν_{max} cm^{-1}: 3400 (-NH- an -OH), 2200 (-CN); 1710 (ester >C=O); 1150, 105 (—C—O stretching); 1050, 735 (1,2-disubstitute phenyl nucleus) UV (EtOH) λ_{max}: 226 and 285 nr (log ϵ: 4.38 and 3.82) 80 MHz ^{1}H-nmr ($CDCl_3$ δ: 1 13 (3H, t, J=7.5 Hz; -OCH_2CH_3); 1.65 (3H d with fine splitting, J=7.0 Hz; >C=CH-CH_3) 2 58 (3H, s; CO_2CH_3); 4.16 (2H, q, J=7 5 Hz -OCH_2CH_3); 4 82 (1H, d of d, J_1=11.0 Hz, J_2= 5 0 Hz; C-3-*H*); 5.42 (1H, q, J=7.0 Hz >C=C*H*-CH_3); 7.55 - 7.01 (4H, m; aromati protons); 8.04 (1H, br s, disappeared on deutera tion; indole -N*H*-).

6b was isolated as an yellowish powder, $C_{24}H_{29}N_3O_4$, m.p. 133-35°, $[\alpha]_D + 46.1°$ (EtOH). Found C, 68.26; H, 7.01; N, 9.82. $C_{24}H_{29}N_3O_4$ require C, 68.07; H, 6.90; N, 9.92%. MS [m/e (%)]: 42 (M^+, 8), 393(8), 377(5), 364(5), 318(5), 205(15 200(70), 193(18), 191(72), 188(15), 174(20), 157(20

156(100), 133(15) 130(70). IR ν_{max} cm^{-1} : 3400 (-OH and -NH-) ; 2215 (CN) ; 1725 (ester >C=O) ; 1160, 1075 (—C—O stretching) ; 1075, 745(1,2-disubstituted phenyl nucleus). UV (EtOH) λ_{max}: 226, 283 and 291 nm (log ε : 4.37, 3.77 and 3 72). 80 MHz ^{1}H-nmr ($CDCl_3$) δ : 1.17 (3H, t, J = 7 7 Hz ; OCH_2-CH_3) ; 1.64 (3H, d of d, J_1=6 6 Hz, J_2= 1.5 Hz ; >C=CH-CH_3) ; 2.34 (3H, s ; -CO_2CH_3) ; 4.30 (2H, q, J=7.7 Hz ; -OCH_2-CH_3) ; 4 61 (1H, d of d, J_1=11 0 Hz, J_2=2 5 Hz ; C-3-H) ; 5.59 (1H, q, J=6.6 Hz ; >C=CH-CH_3) ; 7.45-6.94 (4H, m, aromatic protons), 8.22 (1H, br s, disappeared on deuteration ; indole -NH-).

Ring closure reactions of **6a** *and* **6b** : The ring closure reactions of **6a** and **6b** were studied with glacial AcOH under the same conditions as used in the case of **2a** and **2b**. TLC analysis of the reaction products showed the presence of complex mixtures including substantial amounts of unreacted **6a** and **6b**.

Preparation of **7** : A mixture of **6a** and **6b** (50 mg ; 0 12 mmole) (crude mixture of products from previous reaction) was dissolved in 10 ml of CH_2Cl_2 and was kept in an ice-salt bath Equimolar amount of *t*-BuOCl (13 2 mg ; 0 12 mmole) in 10 ml of CCl_4 was added to the reaction mixture over a period of 1 hr. After addition was complete the solution was stirred for 30 min with no external cooling The yellow solution was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure to give a viscous deep brown mass. This mass was then dissolved in 1% glacial AcOH in 70% MeOH-H_2O, heated at refluxing temperature under nitrogen atmosphere for 3 hr. The methanol was removed from the reaction mixture under reduced pressure and the product was isolated following the usual procedure The resulting product on preparative tlc on silica gel chromatoplates using benzene-ethyl acetate (1 . 1) as the developing system afforded **7** as an yellow amorphous solid, $C_{22}H_{23}N_3O_4$ (M^+ 393) (yield : 10 mg ; *ca* 22%). Found : C, 66.9 ; H, 5.9 ; N, 10.5. $C_{22}H_{23}N_3O_4$ requires C, 67.2 ; H, 5.8 ; N. 10.7%. IR ν_{max} cm^{-1} : 3460-3260 (-NH- and -OH) ; 2190 (-CN) ; 1730 (ester >C=O); 1705 (α,β-unsaturated >C=O); 1150, 1060 (—C—O— stretching) ; 1060, 750 (1,2-disubstituted phenyl nucleus). UV (EtOH) λ_{max} : 315, 238 and 207 nm 80 MHz ^{1}H-nmr ($CDCl_3$) δ : 1 74 (3H, d of d, J_1=6 8 Hz, J_2=1 3 Hz ; >C=CH−CH_3) ; 3.73 (3H, s ; CO_2CH_3) ; 5 64 (1H, q, J=6 6 Hz ; >C=CH−CH_3) ; 7 04-7 35 (3H, m ; 3 aromatic protons) ; 7.66-7.76 (1H, m ; one aromatic proton) ; 9.20 (1H, br s, disappeared on deuteration ; indole -NH-).

Acknowledgement

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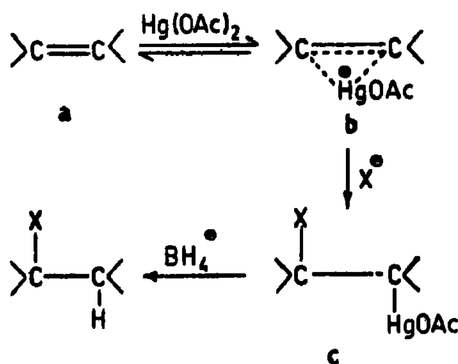
Steric Effects on Oxymercuration : Oxymercuration-Demercuration of Taraxasteryl, Pseudo-Taraxasteryl, and 19-*Epi*-Taraxasteryl Acetates†

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Contrary to usual expectation, taraxasteryl acetate (1b) and pseudo-taraxasteryl acetate (2b) were found to be totally insensitive to normal oxymercuration. This has been rationalised as being due to the steric effects of the 19- and 17-methyl groups on the formation of intermediate mercurium ions, and on the nucleophile attacking these species Conformational analysis of 1b shows that its ring E is not a normal chair, but assumes a twisted conformation due to severe nonbonded interaction between the 12-methylene and the 19-methyl group. Both 1b and 2b, however, underwent oxymercuration-demercuration with allylic rearrangement to give the same compound 2c, when heated with $Hg(OAc)_2$ in glacial HOAc. A partial synthesis of 19-*epi*-taraxasteryl acetate (1d) has been achieved by Witting reaction on the 19-*epi*-norketone (4b) formed by base-catalysed epimerisation of 4a which in turn was derived from 1b. The steric effects providing the driving force for this unconventional epimerisation of 4a to 4b have been explained and supported by comparative ^{13}C nmr spectral analysis of 4a and 4b. Unlike 1b and 2b, 19-*epi*-taraxasteryl acetate (1d) underwent normal oxymercuration. The stereochemical aspect of this reaction has been discussed.

OXYMERCURATION-demercuration of cyclic and acyclic olefins leading to addition across the double bond is a well known reaction[1]. It has been assumed[2,3] that the reaction is initiated by a rapid equilibration of the olefin (a) with an unstable mercurium ion (b), followed by rate- and product-determining attack by a nucleophile $X^{\ominus}$ (Scheme I). Reductive demercuration of the resultant adduct (c) gives the final product often with



Scheme I

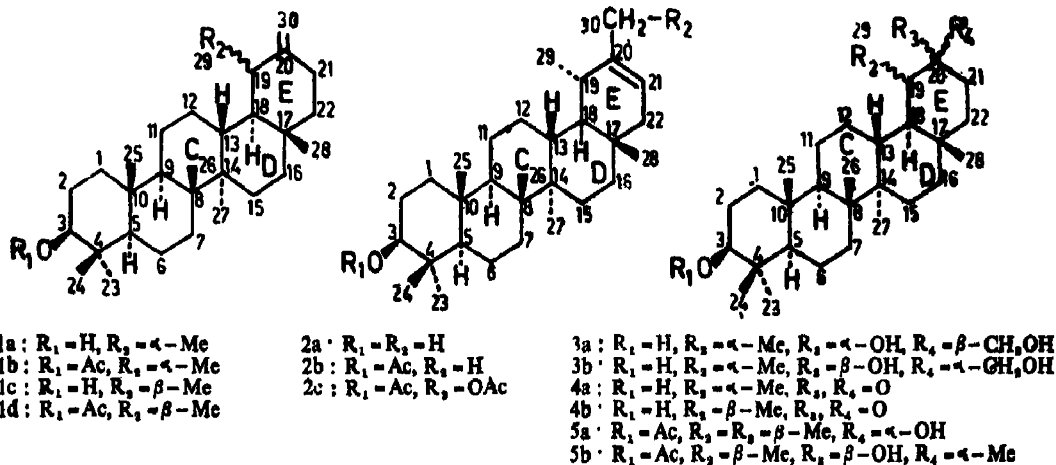
predictable stereoselectivity. Based on this premise it would be interesting to study the steric effects of appropriate functional groups in the olefinic substrates, which might retard or inhibit the preequilibrium formation of the species b, or which, in cases where rapid equilibration is ensured, are expected to govern the stereochemical profile of the final addition products. The results of oxymercuration-demercuration of several substituted methylenecyclohexanes reported recently by Senda *et al*[3] have provided some useful information regarding the stereochemistry of this reaction. The stereochemical aspects of this reaction in a methylene *trans*-octalin system is reflected in the products with (−)-γ-cadinene[4] bearing an exocyclic methylene and a trisubstituted endocyclic double bond.

In course of our chemical investigation of the Indian medicinal plant, *Launaea nudicaulis*[5], we have been able to isolate, in fairly good yield, the pentacyclic triterpene, taraxasterol (1a) bearing a methylenecyclohexane moiety. Acid-catalysed isomerisation[6] of 1a afforded pseudotaraxasterol (2a) possessing a trisubstituted endocyclic double bond. Individually these two compounds contain one or the other type of olefinic functions present in γ-cadinene, but differ essentially from the latter by having an equatorial methyl group β to the double bond, and thus offer themselves as two interesting olefinic substrates for studying the stereochemical aspects of oxymercuration. Accordingly, taraxasteryl acetate (1b) and pseudo-taraxasteryl acetate (2b) were separately treated with mercuric acetate in THF at ambient temperature and the resultant reaction mixture in each case was then treated with alkaline sodium borohydride. Contrary to expectation, it was found that both 1b and 2b were totally unreactive to mercuric acetate as indicated by their almost quantitative recovery from the worked-up reaction mixture. Carrying out the reaction for a longer period or

†Preliminary accounts of this work were presented in the "Symposium on Recent Trends in Organic Chemistry", Department of Chemistry, University of Calcutta, 1979, Abstracts of papers, p. 17, p. 37; and in the "Symposium on Current Topics in Organic Chemistry", Department of Chemistry, University of Calcutta, 1980, Abstracts of papers, p. 9.

under refluxing condition also failed to bring about any change in 1b and 2b. However, when 1b and 2b were treated with mercuric acetate in glacial acetic acid under reflux, both afforded the same compound A, $C_{34}H_{54}O_4$ (M^{+} 526), m.p. 242°, $[\alpha]_D$ + 66.9° ($CHCl_3$), with concomitant precipitation of metallic mercury. Compound A shows in its ir spectrum bands at 1220, 1240 and 1735 cm^{-1} (OAc). The ^{1}H nmr spectrum of the compound shows the presence of two acetoxy groups (δ 2.05, 6H, s). That one of these is associated with a primary allyl acetate moiety of the type H_3C, H >C=C–CH_2OAc, –CH is indicated by the appearance of a one-proton multiplet at δ 5.6 and a two-proton AB-quartet at δ 4.5 (J=10 Hz). An one-proton multiplet obscured in the above AB-quartet establishes the secondary nature of the other acetoxy function. On the basis of these spectral data and its characteristic mass fragmentation[7], structure 2c was assigned to compound A.

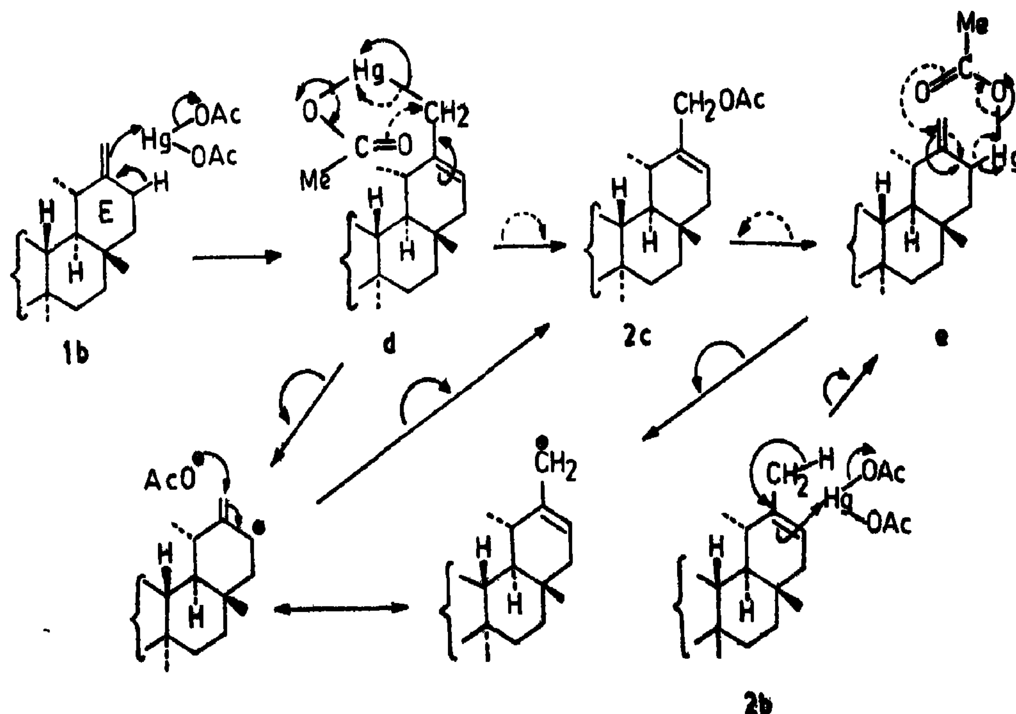
Mechanistically, the formation of 2c from both 1b and 2b may be assumed to be initiated by the generation of the mercurated species d (from 1b) and e (from 2b). Subsequent demercuration of both d and e with concomitant allylic rearrangement gives the same mesomeric cation f (Scheme II, as indicated by ⌒). The latter reacts with acetate anion to give the final product 2c. An intramolecular acetoxylation with simultaneous demercuration (as indicated by ⌒ in d and e) may also be considered as a possible alternative route to 2c.



1a : R_1 = H, R_2 = α – Me
1b : R_1 = Ac, R_2 = α – Me
1c : R_1 = H, R_2 = β – Me
1d : R_1 = Ac, R_2 = β – Me

2a : R_1 = R_2 = H
2b : R_1 = Ac, R_2 = H
2c : R_1 = Ac, R_2 = OAc

3a : R_1 = H, R_2 = α – Me, R_3 = α – OH, R_4 = β – CH_2OH
3b : R_1 = H, R_2 = α – Me, R_3 = β – OH, R_4 = α – CH_2OH
4a : R_1 = H, R_2 = α – Me, R_3, R_4 = O
4b : R_1 = H, R_2 = β – Me, R_3, R_4 = O
5a : R_1 = Ac, R_2 = R_3 = β – Me, R_4 = α – OH
5b : R_1 = Ac, R_2 = β – Me, R_3 = β – OH, R_4 = α – Me



Scheme II

The total insensitivity of **1b** towards normal oxymercuration may be explained by a prior conformational analysis of the compound. Construction of Dreiding model shows that **1b** cannot have a normal chair conformation of its ring E (as in **5**) due to severe steric interaction of the 19-methyl group with the 12-methylene. The presence of such steric strain was also indicated by the chemical shift of the 19-methyl carbon of **1b** and some of its derivatives[5]. This should result in considerable deformation of ring E which would be expected to assume a twisted conformation as shown in **6**. It is believed that **1b** would react with mercuric acetate in this conformation. An examination of the steric effects of the 17- and 19-methyl groups on the two possible transition states leading to the ≺- and β-mercurium ions **7a** and **7b**, respectively, and on the subsequent attack by nucleophile on these species would probably account for this unusual behaviour of **1b**. It is difficult to conceive the formation of a β-mercurium ion **7b** due to its severe interaction with the 17-methyl group, although attack by a nucleophile on this species from the ≺-side is free from any appreciable steric interference. On the other hand, the approach of a nucleophile from the β-side on the ≺-mercurium ion **7a**, assumed to be formed relatively slowly due to some steric effect of the 19-methyl, is prevented by the steric hindrance offered by the 17-methyl group. The net effect would therefore be the observed nonreactivity of **1b** towards oxymercuration. A similar explanation would also apply for the identical behaviour of **2b**.

With a view to establishing the validity of the above conclusion it was decided to study oxymercuration-demercuration on 19-*epi*-taraxasteryl acetate (**1d**) which would be expected to have a normal chair conformation of its E ring (as in **8**) due to the absence of any steric strain between 12-methylene and 19-methyl groups. Consideration of the steric effects in **1d** shows that it should undergo facile oxymercuration. Accordingly, **1d** was prepared from **1b** by the following sequence of reactions. Treatment of **1b** with OsO_4 following the method[6a] used earlier for structurally similar compound afforded a mixture of two epimeric triols, one of which being formed in large excess over the other. The more polar major triol, $C_{30}H_{52}O_3$ ($M^{+\cdot}$ 460), m.p. 260° [ν_{max} 3400 cm^{-1} (OH) ; δ_{ppm} 3.35, 2H, AB q (–C–CH_2OH) and 3.15, 1H, m (>C*H*OH)] and the less polar minor isomer, m p. 223° [ν_{max} 3400 cm^{-1} (OH) ; δ_{ppm} 3.55, 2H, ill-resolved AB q (–C–CH_2OH) and 3.2, 1H, m (>C*H*OH)] were assigned the structures **3a** and **3b**, respectively, on the basis of their various spectral data including those of their mass and the ^{13}C nmr of 3,30-O,O-diacetyl derivative (**B**) of the major triol (Table 1). The stereochemical assignments of the triols are based on a consideration of the stereochemistry of the intermediate osmic esters. It is interesting to note that the earlier workers[6a] reported the formation of a single product in the above reaction of a structurally similar compound.

TABLE 1—CARBON SHIFTS[a] OF 4a, 4b AND COMPOUND B

	4a	4b	Compound B		4a	4b	Compound B
C-1	38 7	38.6	38.2	C-17	34.1	34.5	35.4
C-2	27.3	27.5	23.6	C-18	49.8	49.5	47.2
C-3	78.8	78.5	80.9	C-19	46.0	45.2	40.8
C-4	38.9[b]	38.7[b]	38.0[b]	C-20	218.0	216.0	78.51
C-5	55.3	55.2	55.1	C-21	33.1	33.6	28.3
C-6	18.2	18.2	18.1	C-22	36.3	34.6	39.3
C-7	33.9	33.8	34.2	C-23	27.9	27.9	27.8
C-8	40.8	40.7	41.2	C-24	16 8[d]	17.0[d]	16.4[d]
C-9	50.3	50.1	49.2	C-25	15.8[d]	15.8[d]	16.0[d]
C-10	37.0[b]	36.9[b]	36.8[b]	C-26	16.2[d]	16.1[d]	16.2[d]
C-11	21.1	20.8	21.4	C-27	14.5	14.3	14.6
C-12	25.6[c]	23.9	26.4[c]	C-28	21.8	17.8	20.9
C-13	37.5	37.0	38.8	C-29	15.3	14 7	18.4
C-14	41.7	41.2	42.9	C-30	—	—	65.08
C-15	26.5[c]	26.5	27.8[c]	-O-C(=O)-CH$_3$	—	—	170 8 171 5
C-16	36.0	34 8	37 6	-O-C(=O)-*C*H$_3$	—	—	21 2

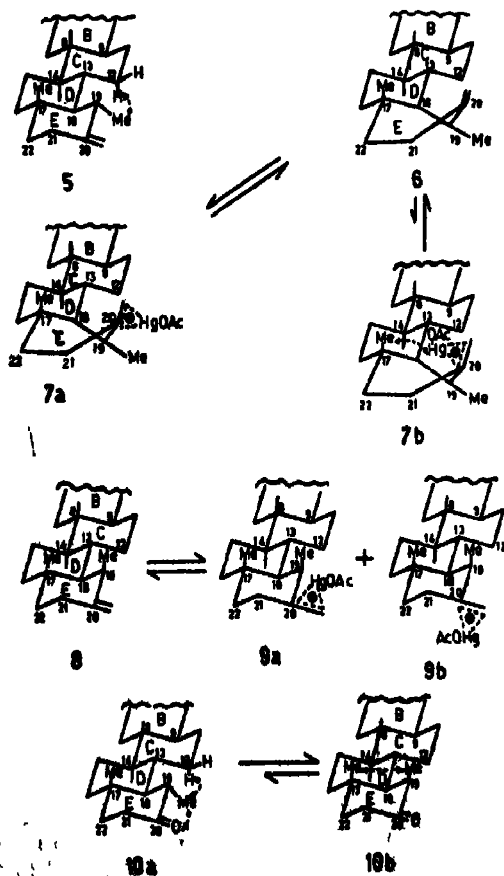
a—values are in ppm downfield from TMS ; $\delta_{(TMS)} = \delta_{(CDCl_3)} + 76.9$ ppm

a,b,c,d—values bearing the same superscript may be interchanged.

Periodate oxidation of both **3a** and **3b** afforded the norketone, $C_{29}H_{48}O_2$ (M^+: 428), m.p. 262° $[\alpha]_D$+59.43° ($CHCl_3$), which from its ir [ν_{max} 338 (OH) and 1700 (>C=O) cm^{-1}]. pmr [δ_{ppm} 3,1 1H, m (>C*H*OH), 2.40, 3H, m and 1.1, 3H, d J=7 Hz (*M*e-C*H*-C(=O)-C*H*$_2$-CH$_2$-)] and mass spectra data was shown to have the structure **4a**. The ^{13}C nmr spectrum of the compound (Table 1) is also in accord with this structure.

The next step in the proposed partial synthesis of **1d** involved the base-catalysed isomerisation of **4a** to its C-19 epimer **4b**. From a naive consideration of thermodynamic stability, such epimerisation would seem to be impossible since in absence of other compelling factors cyclohexanones with an equatorial ≺-methyl is thermodynamically more stable than its isomer bearing an axial methyl at the ≺-position. The unique feature of steric interaction existing in **4a** fortunately helped to reverse the direction of epimerisation in the most unconventional manner to give the 19-*epi*-norketone **4b**. A convincing rationale for this unprecedented transformation emerges from a comparison of the significant nonbonded interactions present in the C, D and E rings of **4a** and **4b** as shown in their conformational expressions **10a** and **10b**, respectively (Scheme III). In **10a** the interactions between the 19-methyl and the 12-methylene and the carbonyl group (at C-20) taken together are clearly greater then the 1,3-diaxial interaction between the 17- and 19-methyl groups in **10b**, and this actually provides

the driving force for the conversion of 4a to 4b. Thus adsorption of 4a on basic alumina[**] followed by elution of the material after 3 days afforded an equilibrium mixture of 4a and 4b in a ratio of about 60 : 40. The same could be achieved by treatment of 4a with ethanolic alkali or with sodium methoxide in dry methanol. The product obtained as a microcrystalline solid after repeated crystallisations from petrol-EtOAc, m.p. 242°, showed a single iodine-staining spot on thin-layer chromatograms run in different solvent systems, and had the same R_f value as that of the starting material. Although it was initially thought to be a pure sample of the isomeric norketone 4b from a comparison of its physical constants, ir, pmr and mass spectral data with those of 4a, a ^{13}C nmr spectral analysis of the isomerised product clearly indicated the presence of 4a as a minor component in this material. Comparison of the ^{13}C nmr spectrum of this reaction product with that of pure 4a shows that the former contains two sets of signals, one of which corresponds to the carbon atoms of pure 4a. The additional signals (Table 1) must therefore be due to the carbon atoms of a new compound which has most of its carbon resonances almost coinciding with those of 4a. The essential differences in the carbon shifts of pure 4a and those of the pure isomerised product 4b, as obtained by the above subtraction process, may be well accounted for in terms of the changed additivity parameters attendant with epimerisation at C-19 of 4a producing 19-*epi*-norketone 4b (10a ⇌ 10b).[7] Thus the release of the steric strain between the 12-methylene and the equatorial 19-methyl group (C-29) in 4a owing to latter changing to 4b (with an axial 19-methyl group) is accompanied by an expected downfield shift of C-12 of 4b by 1.7 ppm. A corresponding deshielding of the 19-methyl carbon (C-29) of 4b is, however, not observed due to a newly generated shielding effect arising out of the 1 : 3-diaxial interaction between the 17- and 19-methyl groups of 4b. But this interaction in turn has resulted in the expected shielding of C-28 (17-methyl) of 4b by 4 ppm (Table 1). These spectral data thus strongly support the structure of the isomeric product to be the C-19 eipmer of 4a. But all attempts to isolate 4b in the pure state by repeated fractional crystallisations of the mixture from different solvents or by repeated column chromatography and even by carrying out these processes on the acetylated mixture were unsuccessful. So the above mixture of 4a and 4b were subjected to Wittig reaction with the ylid prepared from methyltriphenylphosphonium iodide in presence of NaH in DMSO. This has yielded a mixture of two triterpenoids in extremely poor yield. One of these was identified with taraxasterol (1a) while the other, separated from 1a by repeated column chromatography, $C_{30}H_{50}O$ ($M^{+\cdot}$ 426), was shown to be the desired 19-*epi*-taraxasterol (1c) from its pmr and mass spectral data which were strikingly similar to those of 1a. The acetyl derivative of 1c was then subjected to oxymercuration-demercuration reactions. Unlike 1b and 2b, treatment of 19-*epi*-taraxasteryl acetate (1d) with mercuric acetate in aqueous THF at ambient temperature followed by borohydride reduction of the resultant reaction mixture afforded two compounds C and D in the ratio of about 3 : 1. Due to extremely low yield of 1c in the Witting reaction, it has not been possible to prepare these compounds in amounts sufficient to carry out detailed studies on them except mass spectral analysis, which, however, suggests the isomeric structures 5a and 5b for the two compounds, the stereochemistry at C-20 remaining undefined. The formation of 5a and 5b may be explained as the result of normal oxymercuration of 1d, which can equally form the α- and β-mercurium ions 9b and 9a, respectively (Scheme III). Consideration of the steric effects on the nucleophile attacking the species 9a and 9b suggests that the major compound (C) should have the stereochemistry at C-20 as shown in 5a, while the minor product (D) should have the opposite stereochemistry at this centre as in 5b.



Scheme III

The above investigations on 1b, 2b and 1d thus provide significant information regarding steric effects on oxymercuration of olefinic compounds.

Experimental

Melting points were determined in a Kofler block and are uncorrected. IR spectra were run in KBr disc in a Beckman-Infrared spectrophotometer (Model 20). ^{1}H nmr spectra were mostly recorded in an 80 MHz Varian CFT-20 instrument

in $CDCl_3$ solution using TMS as the internal standard, and the chemical shifts are expressed in δ_{ppm}. The ^{13}C nmr spectra were also run in the same instrument using a 20MHz oscillator in $CDCl_3$ and with the same internal standard. The substitution profile of carbon centres were determined by off-resonance decoupling technique (SFORD). Mass spectra were run in an AEI MS9 instrument equipped with a direct inlet system and operating at 70 eV. The figure in first bracket attached to each m/e value indicates relative intensity which is abbreviated as r.i. Silica gel (60-100 mesh) was used for column chromatography and silica gel G for tlc performed at room temperature (25-35°). All analytical samples were routinely dried over P_2O_5 at 55-138° depending on the m.p. of the compounds for 24 hr *in vacuo*. Anhydrous Na_2SO_4 was used for drying organic solvents and petrol used had b.p. 60-80°.

Attempted oxymercuration-demercuration of **1b** *and* **2b**: Taraxasterol (**1a**) isolated from the petrol extract of *Launaea nudicaulis*[5] was acetylated in the usual manner to give **1b**, crystallised from $CHCl_3$-MeOH (1 : 9), m.p. 239-40°, $[\alpha]_D$ +94.5° ($CHCl_3$). **1b** was isomerised with 10% ethanolic H_2SO_4 following the previously reported method[6] to give **2a** which was acetylated with Ac_2O/py to give **2b**, crystallised from $CHCl_3$-MeOH (1 : 9), m p. 228°, $[\alpha]_D$ +51.8° ($CHCl_3$).

To a solution of $Hg(OAC)_2$ (0.065 g) in H_2O (1 ml) and THF (3 ml) was added a solution of **1b** (0.09 g) in THF (2 ml) at r.t. (25°) and the mixture was stirred for 5 hr. At first a yellow suspension was formed, which did not disappear even at the end of the reaction period. The reaction mixture was then treated with 5 ml of 3*M* NaOH followed by 15 ml of a solution of 0.5*M* $NaBH_4$ in 3*M* NaOH. It was stirred for about 15 min and then filtered, the residue washed with THF The combined filtrate was saturated with NaCl and extracted with THF, dried and the solvent removed. The residue crystallised from $CHCl_3$-MeOH (1 : 9) to give unreacted **1b** (0.085 g). TLC of the total reaction product did not show any spot other than those corresponding to **1b** and a trace of **1a**.

Pseudo-taraxasteryl acetate (0.09 g) was also treated with Hg(OAc) in aqueous THF in the above proportion and in the same manner. Treatment of the reaction mixture with alkaline $NaBH_4$ and working up in the above manner gave unreacted 2b (0.085 g). Here again tlc of the total reaction product did not show any spot other than those corresponding to 2b and a trace of 2a.

Both **1b** (0.045 g) and **2b** (0.045 g) were separately treated with $Hg(OAc)_2$ in THF and the mixture in each case was stirred at refluxing temperature for 2 hr. Treatment of the reaction mixture in each case with alkaline $NaBH_4$ followed by usual work-up gave unreacted starting material and trace of the corresponding deacetyl derivative.

Reaction of **1b** *and* **2b** *with* $Hg(OAc)_2$ *in glacial HOAc*: A solution of **1b** (0.236 g) in HOAc (10 ml) was treated with $Hg(OAc)_2$ (0.15 g) dissolved in HOAc (1 ml). The mixture was then refluxed on a magnetic stirrer for 4 hr. The reaction mixture was filtered while hot to free it from deposited metallic mercury. The filtrate, after dilution with water, was extracted with $CHCl_3$, washed, dried and the solvent removed. The residue was chromatographed. The petrol-EtOAc (100 : 1) eluate gave unchanged **1b** (0.035 g). Further elution of the column with petrol-EtOAc (50 : 1) afforded **2c** crystallised from petrol-EtOAc mixture, m.p. 242°, $[\alpha]_D$ + 66.9° ($CHCl_3$). Found: C, 77.50; H, 10.2[illegible]. $C_{34}H_{54}O_4$ requires C, 77.56; H, 10.26%. ν_{max} 1220, 1240 and 1735 cm^{-1} (OAc); δ_{ppm}: 5.6, 1H, [illegible] (>C=C*H*-CH$_2$-); 4.5, 2H, AB q (–CH=C-C*H*$_2$-OAc); 4.5, 1H, m obscured in the above signal (>C*H*OAc); 2.05 6H, s (-OCOC*H*$_3$); 0.72-1.0[illegible] (7 C-methyls); m/e (r.i.); 526 (M$^{+\cdot}$, 3), 484 (12), 466(99.8), 386(5), 324(12), 249(46), 216(44), 189(100), 187(99.9), 173(47), 135(99.5), 107(99.9), 95(99), 81(98) and 69(99).

In an identical manner **2b** (0.05 g) was treated with $Hg(OAc)_2$ (0.03 g) in glacial HOAc. The reaction product was worked up as above and chromatographed. The petrol-EtOAc (80 : 1) eluate gave unchanged **2b** (0.008 g), while the petrol-EtOAc (50 : 1) eluate afforded a solid (0.04 g), crystallised from the same solvent mixture, m.p. 242°. It was found to be identical in all respects with **2c**.

Preparation of the triols **3a** *and* **3b** *from* **1b**: Following the method used earlier[6a] for structurally similar compound, **1b** (1.9 g) dissolved in a mixture (1 : 1) of dry pyridine and $CHCl_3$ (100 ml) was treated with OsO_4 (1 g) and the solution was kept at 20° for 7 days. Removal of solvent under reduced pressure gave a dark residue which was heated under reflux for 3 hr with benzene (45 ml), MeOH (45 ml) and a mixture of KOH (10.5 g) and mannitol (10.5 g) in EtOH (45 ml) and water (28 ml). The solvent was then removed under reduced pressure and the residue was diluted with water, extracted with ether after saturating the solution with NaCl. The ether extract was dried, evaporated and the residue was chromatographed over Brockmann alumina. The petrol-EtOAc (10 : 1) eluate gave **1a** (0.05 g). Further elution of the column with 5% methanolic $CHCl_3$ gave the mixture of triols **3a** and **3b** (total yield 0.75 g). The mixture was then rechromatographed over alumina. The early fractions of the 5% methanolic $CHCl_3$ eluate, on evaporation, gave a solid which crystallised from petrol-EtOAc to give the pure less polar triol **3b** (0.05 g), m.p. 223°, R_f 0.4 in MeOH-$CHCl_3$ (1 : 1) as the developer. Found: C, 78.30; H, 11.33. $C_{30}H_{52}O_3$ requires C, 78.26; H, 11.30%. ν_{max} 3400 cm^{-1} (OH); δ_{ppm}: 3.55, 2H, AB q, J=10 Hz (–C–C*H*$_2$OH); 3.2, 1H, m(>C*H*OH) and 0.75–1.05 (7 C–methyls); m/e (r.i.): 460(M$^{+\cdot}$, 6), 442(5.5), 429(38.9), 411(19.3) 373(25.8), 355(20), 216 (17.1), 207(81.2), 205(22.5), 191(30.5), 189(100), 187(21), 81(73.5) and 69(82.9).

The later fractions of the 5% methanolic $CHCl_3$ eluate in the above chromatography afforded a solid which crystallised from petrol-EtOAc to give the pure more polar triol **3a** (0.69 g), m.p. 260°, R_f 0.35 with MeOH-$CHCl_3$ (1 : 1) as the developer. Found : C, 78.20 ; H, 11.41. $C_{30}H_{52}O_3$ requires C, 78.26 ; H, 11.30%. ν_{max} 3400 cm^{-1} (OH) ; δ_{ppm} : 3.35, 2H, AB q, J=10 Hz ($-\overset{|}{\underset{|}{C}}-CH_2OH$) ; 3.15, 1H, m (>CHOH) and 0 7−1.0 (7 C-methyls) ; m/e (r.i.) : 460 (M^+, 5), 442(5), 429(37), 411(19), 373(26), 355(19), 216(17.5), 207(82), 205(23.5), 191(51.1), 189(100), 187(21.2), 81(73.4) and 69(81.8).

Formation of the norketone **4a** : The mixture of the triols **3a** and **3b** (0.75 g) dissolved in EtOH (320 ml) was treated with a solution of sodium metaperiodate (0.55 g) in water (5 5 ml). The mixture was kept at 20° for 16 hr. EtOH was removed under reduced pressure and the residue was treated with water (30 ml), extracted with ether and dried Removal of solvent gave a solid (0.47 g) which on repeated crystallisations from petrol-EtOAc afforded pure **4a**, m.p. 262° ; R_f 0.4 with petrol-EtOAc (4 : 1) as the developer. Found : C, 81 2 ; H, 11.24. $C_{29}H_{48}O_2$ requires C, 81.30 ; H, 11.21% ν_{max} 3380 (OH) and 1700 (>C=O) cm^{-1} ; δ_{ppm}: 3.15 1H, m (>CHOH) ; 2.40, 3H, m (Me−$\underset{|}{C}H$−$\overset{O}{\overset{\|}{C}}$−$CH_2$−$CH_2$−) ; 1.1, 3H d, J=7Hz(*Me*−$\underset{|}{C}$H−$\overset{O}{\overset{\|}{C}}$−) and 0 71−1.0 (6 C-methyls) ; m/e (r.i.) : 428 (M^+, 17.5), 410(63.5), 395 (40.9), 367(25.1), 341(10.7), 328(29.3), 259(10.8), 207(41), 189(100), 136(77 8), 135(76.3), 123(60.6), 121(64 7), 109(55.5), 95(77.9), 81(65.9) and 69(61.8).

Epimerisation of **4a** : A solution of **4a** (0.35 g) in $CHCl_3$ was adsorbed on Brockmann alumina in a column and kept for 3 days. The material was then eluted with $CHCl_3$. Removal of solvent gave a solid (0.34 g) which on repeated crystallisations from petrol-EtOAc afforded a microcrystalline material, m.p. 242°, having R_f value same as that of **4a**. The ir, pmr and mass spectra of this material were very similar to those of **4a**. It was shown to be a mixture of **4a** and **4b** by comparison of its ^{13}C nmr spectral data with those of pure **4a**.

Wittig reaction on the mixture of **4a** *and* **4b** : A solution of equimolecular amounts of ϕ_3P (7.86 g) and CH_3I (4.26 g) in perfectly dry $CHCl_3$ (25 ml) was refluxed for 1 hr. Removal of solvent left an oily residue which was treated with dry ether when a gummy solid separated out. The crude solid was crystallised from Et_2O-MeOH to give pure methyltriphenylphosphonium iodide (4.5 g), m.p. 181-83°. It was dried in vacuum desiccator.

A 50 ml r.b. flask equipped with a dropping funnel (with pressure-equaliser device), a reflux condenser and a nitrogen-inlet tube was placed on a magnetic stirrer. The whole system was repeatedly flushed with dry, oxygen-free nitrogen. Oil-free NaH (0 75 g) was introduced into the flask and to it was added dry DMSO (6 ml) through the dropping funnel The mixture was heated at 75-80° for 2 hr in dry, oxygen-free nitrogen atmosphere until the evolution of hydrogen ceased. The resultant solution was then cooled in ice-bath and to this was added dropwise through the dropping funnel a solution of $\phi_3\overset{\oplus}{P}CH_3\overset{\ominus}{I}$ (2 g) in DMSO (10 ml). The reaction mixture was stirred for 30 min at room temperature. To this was added dropwise from the dropping funnel a solution of 0 25 g of the mixture of **4a** and **4b** in DMSO (30 ml). The reaction mixture was then heated at 60-70° for 40 hr. The product was decomposed with ice-cold water (saturated with NaCl), extracted with ether, washed with brine and dried. Removal of solvent gave a residue which was chromatographed. The petrol-EtOAc (20 : 1) eluate gave a mixture of **1a** and **1c** (0.03 g). The mixture was rechromatographed. The early fractions of petrol-EtOAc (25 : 1) gave **1a** (0.011 g), R_f 0.45 in petrol-EtOAc (6 : 1) as the developer. The later fractions of the same eluate gave pure **1c**, (0.017 g), R_f 0.40 in petrol-EtOAc (6 : 1) as the developer. Found : C, 84.48 ; H, 11.78. $C_{30}H_{50}O$ requires C, 84.51 ; H, 11.73%. δ_{ppm} : 4.7, 2H, m ($-\underset{|}{C}=CH_2$) ; 3.06, 1H, m (>CHOH) and 0.77-1.2 (7 C-methyls) ; m/e (r.i.) : 426(M^+, 12.3), 357(4.6), 218(12.3), 207(53.8), 189(100), 149(95), 109(99.1), 107(90), 81(98 9) and 69(95).

Oxymercuration-demarcuration of **1d** : **1c** (0.012 g) was acetylated with Ac_2O/py in the usual manner. The product crystallised from MeOH-$CHCl_3$ (9 : 1) to give **1d**, m.p. 210°. To a solution of 0.007 g of $Hg(OAc)_2$ in 0 2 ml water was added 0.8 ml THF, when a yellow suspension was formed. To this was added a solution of **1d** (0.01 g) in THF (2 ml) and the mixture was stirred for 1 hr. Within a few minutes the yellow suspension became almost clear. The reaction mixture was treated with 1 ml of 3*M* NaOH followed by 3 ml solution of 0.5*M* $NaBH_4$ in 3*M* NaOH, and stirred for 15 min. The mass was filtered and the filtrate was saturated with NaCl, extracted with THF and dried. Removal of solvent gave a white residue which was chromatographed. The early fractions of petrol-EtOAc (10:1) eluate gave **5b** (0.002 g), crystallised from MeOH-$CHCl_3$ (9 : 1), m.p. 200°, R_f 0.5 in petrol-EtOAc (3 : 1) as the developer. M/e (r.i) : 486(M^+, 4), 468(10.2), 207(100), 189(94.5), 135(95.3), 123(50.4), 121(40.5), 109(99.1) and 107(65.1).

The later fractions of the petrol-EtOAc (10 : 1) eluate in the above chromatography afforded **5a** (0.006 g), crystallised from MeOH-$CHCl_3$ (9 : 1), m.p. 170°, R_f 0.4 in petrol-EtOAc (3 : 1) as the developer. M/e (r.i) : 486(M^+, 4.5), 468(15.8), 207(98.1), 189(100), 135(93.1), 123(55.5), 121(45.5), 109(98.1) and 107(68.1).

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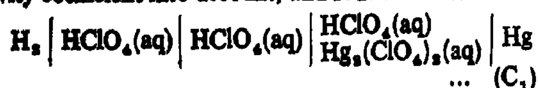
Standard Electrode Potential of Mercury-Mercurous Electrode at a Number of Temperatures

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From the study of the cell ; Pt Q.H. (sat.) $HClO_4(c_1)|HClO_4(c_1)|\begin{matrix} HClO_4 & (c_1) \\ Hg_2(ClO_4) & (c_2) \end{matrix}|Hg$, the standard electrode potential of mercury-mercurous electrode has been determined from 5° to 35° at 5° intervals. Over this range of temperatures the results can be expressed by the equation, $E_t = 0.80252 - 2.51 \times 10^{-4}t - 1.0668 \times 10^{-6}t^2$ $\Delta H°$, $\Delta G°$ and $\Delta S°$ of the reaction $Hg_2^{2+} + H_2 = 2Hg + 2H^+$ have also been calculated.

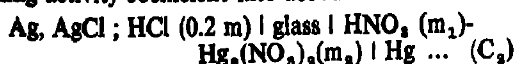
THE standard electrode potential of mercury-mercurous was first determined by Linhart[1] by using the cell (C_1) at 25°, without taking the activity coefficient into account, and found as 0.7926v.



$$H_2 \left| HClO_4(aq) \right| HClO_4(aq) \left| \begin{matrix} HClO_4(aq) \\ Hg_2(ClO_4)_2(aq) \end{matrix} \right| Hg \quad \ldots \quad (C_1)$$

Lewis and Randall[2] revised the value of Linhart to 0.7986 int. volt by taking activity coefficient into account. By plotting the original data of Linhart in a $\mu^{\frac{1}{2}}$ diagram, Bray and Hershey[3] adopted the value of $E^0_{Hg,Hg_2^{2+}}$ equal to 0.7975 ± 0.0010 int. volt. El Wakkad and Slem[4] found the value of $E^0_{Hg,Hg_2^{2+}}$, by taking activity coefficient into account, to be 0.7988 ab. volt in presence of air and 0.7971 ab. volt in absence of air.

Bonner and Unietis[5] found the $E^0_{Hg,Hg_2^{2+}}$ value as 0.7961 ab. volt at 25° using the cell (C_2) after taking activity coefficient into account.



$$Ag, AgCl \,;\, HCl\ (0.2\ m) \mid glass \mid HNO_3\ (m_1)\text{-}Hg_2(NO_3)_2(m_2) \mid Hg \ \ldots \ (C_2)$$

The discrepancies in the values of $E^0_{Hg,Hg_2^{2+}}$ observed by various workers may be due to two factors viz, (i) the liquid junction potential and (ii) incorrect value of activity coefficient.

In the present work, Linhart's cell (C_1) with certain modifications was used. For the elimination of liquid junction potential a modification of Owen's[6] procedure was adopted.

Materials and Methods :

Double distilled deoxygenated water was used throughout the experiments. Perchloric acid (AR, 60%) was used and diluted according to requirements. Mercurous perchlorate was prepared by vigorously shaking a mixture of HgO (prepared as recommended by Vogel[7]), deoxygenated double distilled water, excess of (i) mercury and (ii) perchloric acid in absence of air and light. To confirm the completion of the reaction, a few drops of liquid were withdrawn, diluted with deoxygenated double distilled water and treated with excess NaCl and filtered. No Hg^{2+} ion was left in the solution as the filtrate did not give the black colouration with H_2S.

Mercurous perchlorate was estimated by titrating against KBr (AR) as well as NaCl (AR) using bromophenol blue as indicator[7,8]. There was negligible difference in the results. The amount of free $HClO_4$ in the solution was estimated by taking a known volume of the solution into a measuring flask and adding a slight excess of NaCl (AR). The mercurous ions in the solution were precipitated as mercurous chloride. The solution in the measuring flask (precipitate not removed) was made upto the mark by adding double distilled water. (A correction in the volume of the solution was made for the volume of insoluble Hg_2Cl_2). The Hg_2Cl_2 settled at the bottom and a portion of the supernatant was titrated against borax using methyl red as indicator.

The cell solutions were prepared in molarity at the experimental temperature from the stock solution of $HClO_4$, and a mixture of $HClO_4$ and $Hg_2(ClO_4)_2$ in deoxygenated double distilled water. The quinhydrone electrode was prepared as described earlier[9] Temperature control was within $\pm 0.05°$. All the cells were studied in duplicate. The difference in the duplicates was less than 0.1 mV The e.m.f. of the cells was measured in ab. volts at hourly interval for at least 3 hr by a Tinsley Vernier potentiometer using a Bajaj mirror galvanometer, type M.G.8. The values of E (ab. volts) given in Tables 1 to 7 represents the mean of the duplicate cells.

TABLE 1

Temperature 5°

$c_1 \times 10^3$ / $c_2 \times 10^4$	10.0249 E	20 0635 E	40.065 E	60.200 E	80.234 E
9.952	0.11171	0.09427	0.07675	0.06624	0.05856
20.076	0.12010	0.10257	0.08521	0.07450	0.06690
30.028	0.12479	0 10732	0.08977	0.07941	0.07186
40.150	0.12816	0.11076	0.09334	0.08275	0.07545
50.103	0.13077	0.11346	0 09601	0.08536	0.07790
q_0 —	0.08702	0.08689	0.08704	0.08712	0.08688



TABLE 2

Temperature 10°

$c_1\times10^3$	10.055	20 149	40.198	60.348	80.465
$c_2\times10^4$	E	E	E	E	E
9 980	0.11475	0 09693	0.07902	0.06828	0 06099
20.131	0.12285	0 10524	0.08725	0.07670	0.06926
30 111	0 12763	0.11016	0.09206	0.08169	0.07420
40.263	0.13123	0.11339	0 09560	0 08481	0.07765
50.243	0 13389	0.11613	0.09806	0.08760	0.08024
q_0	0.08953	0.08961	0.08966	0.08971	0 08986

TABLE 3

Temperature 15°

$c_1\times10^3$	10.005	$c_1\times10^3$	19 902	39 992	60 019	79 981
$c_2\times10^4$	E	$c_2\times10^4$	E	E	E	E
9.990	0.11784	9 990	0.09979	0 08155	0 07074	0 06301
20.000	0.12634	20 054	0 10805	0.08996	0 07925	0 07156
25 160	0.12914	29.970	0 11328	0 09493	0 08423	0 07667
30 044	0.13132	39.960	0 11695	0 09844	0.08784	0.08026
39.960	0.13511	50 024	0.11948	0.10134	0 09068	0.08313
q_0'	0.09193	q_0	0.09203	0 09216	0 09225	0 09230

TABLE 4

Temperature 20°

$c_1\times10^3$	10 042	20.063	40 127	60.190	80.354
$c_2\times10^4$	E	E	E	E	E
10.106	0.12038	0 10235	0.08324	0 07232	0.06413
20.043	0.12904	0 11071	0.09217	0.08082	0 07303
30.151	0 13396	0 11556	0 09717	0.08580	0 07821
40.087	0.13748	0 11901	0.10043	0.08952	0 08180
50.195	0.14032	0 12211	0 10328	0.09250	0 08475
q_0'	0 09428	0 09436	0.09430	0 09417	0.09406

TABLE 5

Temperature 25°

$c_1\times10^3$	9 998	20 005	39.948	60 022	80.000
$c_2\times10^4$	E	E	E	E	E
9 923	0 12317	0 10467	0 08563	0 07423	0 06632
20.017	0 13240	0.11359	0 09471	0 08337	0 07535
29 940	0 13732	0 11845	0 09969	0 08862	0 08030
40 035	0 14105	0 12216	0 10363	0 09227	0 08430
49 958	0.14382	0 12504	0 10624	0 09494	0 08705
q_0	0 09675	0 09691	0.09685	0 09686	0.09698

TABLE 6

Temperature 30°

$c_1\times10^3$	10 016	20 012	40 024	60 036	80 148
$c_2\times10^4$	E	E	E	E	E
10.082	0.12591	0 10712	0 08773	0.07594	0 06776
19 992	0 13467	0.11604	0 09671	0 08508	0 07701
30 074	0 13998	0 12113	0 10224	0.09031	0.08223
39.985	0.14379	0.12477	0 10573	0 09401	0.08603
50.066	0 14662	0.12791	0 10854	0.09718	0 08926
q_0	0.09879	0 09904	0 09897	0 09869	0.09869

TABLE 7

Temperature 35°

$c_1\times10^3$	9.998	20 035	39 970	60 005	80 010
$c_2\times10^4$	E	E	E	E	E
9.923	0 12858	0.10950	0 09003	0 07821	0.07053
20 017	0.13769	0 11869	0.09930	0.08750	0.07957
29.940	0 14290	0.12417	0.10459	0.09281	0 08490
40.034	0 14683	0.12787	0.10840	0.09643	0.08872
49.958	0.14948	0 13066	0.11130	0 09929	0.09165
q_0	0.10131	0.10160	0.10173	0.10175	0.10211

Results and Discussion

The e.m.f. (Stockholm convention) of the cell,

$$\mathrm{Pt} \left| \mathrm{Q.H.\ (sat.)\ HClO_4}(c_1) \right| \mathrm{HClO_4}(c_1) \left| \begin{matrix} \mathrm{HClO_4} & (c_1) \\ \mathrm{Hg_2(ClO_4)_2} & (c_2) \end{matrix} \right| \mathrm{Hg},$$

is given by

$$E = E^o + \frac{RT}{2F} \ln \frac{a_{Hg_2^{2+}}}{(a_{H^+})^2} + \mathrm{l.j.p.} \quad \ldots \quad (1)$$

Applying the expression $-\log f_i = \frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} - B_i\mu$, for the activity coefficient of ions, we get equation (2),

$$E - \frac{2\ 30259RT}{2F}\left[\log\ c_2 - 2\log c_1 + \frac{2A\sqrt{\mu_1}}{1+\sqrt{\mu_1}} - \frac{4A\sqrt{\mu_2}}{1+\sqrt{\mu_2}}\right]$$
$$= E^o_{cell} + \frac{2.30259RT}{2F}[B_2\mu_2 - B_1\mu_1] + \mathrm{l.j.p.} \quad \ldots \quad (2)$$

$HClO_4$ and $Hg_2(ClO_4)_2$ being completely ionized and A being known[10], the L.H.S. in equation (2) was calculated.

At any temperature, the e.m.f. values of five different series of cells were measured. Every series had five sets of cells. In every series c_1 was fixed and c_2 was varied. For the same concentration of $HClO_4$, as c_2 decreases the difference between μ_2 and μ_1 also decreases.

The values of L.H.S. of equation (2) for the same series, when plotted against c_2, gives a straight line (Fig. 1).

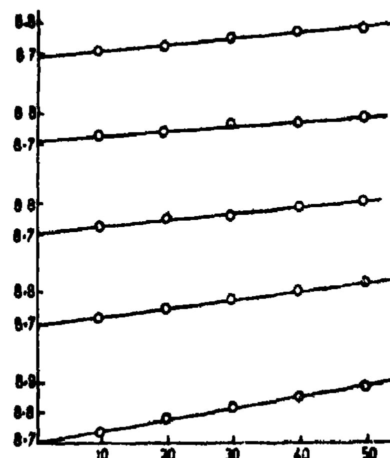


Fig 1. Plot of $q\times10^2$ vs $c_2\times10^4$.
(Temp. 5°; $q = E^o_{cell} + \frac{2.30259\ RT}{2F}(B_2\mu_2 - B_1\mu_1)$l.j.p.)

When $c_2=0$, $\mu_1=\mu_2=c_1$ and l.j.p.$=0$, so that the values of L.H.S., corresponding to $c_2=0$, in the plots (denoted by q_0) is represented by

$$q_0 = E^o_{cell} + \frac{2\ 30259RT}{2F}(B_2 - B_1)\mu_1 \quad \ldots \quad (3)$$

Taking all the five series at any temperature, L.H.S. of equation (3), (denoted by q_0), is plotted

against μ_1, a straight line is obtained (Fig. 2).

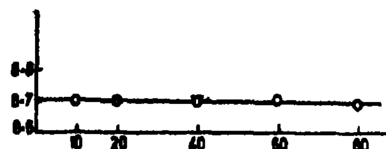


Fig. 2. Plot of $q_o \times 10^3$ vs $\mu_1 \times 10^3$.
(Temp 5° ; $c_o = E^o_{cell} + \frac{2.30259\ RT}{RF}[B_2 - B_1]\mu_1$)

By extrapolation to $\mu = 0$, E^o_{cell} (Stockholm convention) were found out on molarity scale as 0.08707, 0.08949, 0.09191, 0.09439, 0.09679, 0.09898 and 0.10130 at 5, 10, 15, 20, 25, 30 and 35°, respectively.

The conversion of E^o_{cell} on molarity scale to E^o_m on molality scale in these cells are governed by the equation, $E^o_m = E^o_{cell} - \frac{RT}{2F}\ln \rho$, where ρ = density of water. $E^o_{Q.H.}$ is known from literature[11]. Hence $E^o_{Hg,Hg_2^{2+}}$ were found out to be 0.80143, 0.80028, 0.79909, 0.79784, 0.79653, 0.79518 and 0.79377 ab.volt at 5, 10, 15, 20, 25, 30 and 35°, respectively

For check and confirmation at one temperature (25°), the cell $H_2 \mid HClO_4(c_1) \mid HClO_4(c_1) \left| \begin{matrix} HClO_4 & (c_1) \\ Hg_2(ClO_4)_2(c_2) \end{matrix} \right| Hg$ was studied and almost the same value, 0.79663 abs.volt, of $E^o_{Hg,Hg_2^{2+}}$ was obtained.

Thermodynamic functions : The standard potential of the cell,

$$H_2 \left| HClO_4(c_1) \right| HClO_4(c_1) \left| \begin{matrix} HClO_4 & (c_1) \\ Hg_2(ClO_4)_2(c_2) \end{matrix} \right| Hg,$$

can be represented by equation (4).

$$E_t = 0.80252 - 2.51 \times 10^{-4} t - 1.0668 \times 10^{-6} t^2 \quad (4)$$

With the help of equation (4) and other thermodynamic relations, the values of ΔG^o, ΔS^o and ΔH^o at 5 to 35° at 5° interval for the cell reaction, $Hg_2^{2+} + H_2 = 2Hg + 2H^+$ were calculated and are given in Table 8.

TABLE 8

Temp (°C)	$-\Delta G^o$ (cal)	$-\Delta S^o$ cal degree^{-1}mole^{-1}	$-\Delta H^o$ (cal.)
5	36962	12.08	40323
10	36906	12.54	40458
15	36850	13.05	40612
20	36796	13.56	40771
25	36738	14.02	40919
30	36670	14.53	41075
35	36607	15.04	41241

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On the Polarographic Reduction of 2-Aminobenzothiazoles

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2-AMINOBENZOTHIAZOLES are widely used as precursors for the synthesis of compounds of medicinal importance[1-4]. Unlike other heterocycles they do not undergo reduction at the d.m.e., despite their having a reducible C=NH bond. Their polarographic reduction even at higher potential is not achieved by extending the potential range with lithium chloride and tetramethyl ammonium bromide as supporting electrolytes[5,6]. Although it is difficult to explain the highly polarographically inert nature of these thiazoles, it can perhaps be attributed to the high aromaticity developed in them by the phenyl group.

These compounds undergo complex ion formation with transition metals[7] in the *p*H range 2.0 to 6.0. In the higher *p*H range no such reaction takes place and simply the metal hydrous oxides are precipitated. However, when the metal salt solution was added to the thiazole solution in NH_4Cl-NH_4OH buffer (*p*H 9.3) the resulting mixture remained unchanged and could be subjected to polarographic analysis Subsequently, these thiazoles were investigated polarographically using base medium, corresponding to Brdicka solution 0.01 *M* $COCl_2$, 0.1 *M* NH_4Cl and 0 1 *M* NH_4OH.

Realising that no apparent similarity existed in the role of Brdicka solution in the proteins and in our aminobenzothiazoles, the $COCl_2$ in the base electrolyte was replaced with other Lewis acids, e g, nickel, manganese, zinc and aluminium halides. It was found to our much satisfaction that well defined reduction waves, just similar to that in the presence of cobalt chloride, were obtained here.

It may be argued that the above mentioned polarographic waves may be due to the reduction of the metal thiazole complexes, since no possible evidence of complex ion formation on the basis of spectrophotometric and electrometric techniques was forthcoming, and the half wave potentials of metals and their complexes with ammonia are quite different from the $E_{\frac{1}{2}}$ of Brdicka solution[8]. Interestingly enough, the $E_{\frac{1}{2}}$ of 2-aminobenzothiazoles in Co^{2+} and Ni^{2+} ammonical solutions are more positive than those of the metal and the corresponding metal amine complex (Table 1) Furthermore, shift in half-wave potential of 2-ABT with various substituents and a good correlation between $E_{\frac{1}{2}}$ and σ (Fig. 1) strongly support the view that 2-aminobenzothiazoles alone were undergoing reduction at d.m.e

TABLE 1—HALF-WAVE POTENTIALS OF METAL IONS, THEIR AMMONIUM COMPLEXES[8] AND 2-ABT IN RESPECTIVE METAL ION IN AMMONICAL SOLUTIONS

Metal ion	$-E_{1/2}$, V	Metal ion +2-ABT	$-E_{1/2}$, V	Metal amines	$-E_{1/2}$, V
Co^{2+}aq.	1.29	Co^{2+}aq. +2-ABT	1.12	$Co(NH_3)_5H_2O$	1.40
Ni^{2+}aq.	1.10	Ni^{2+}aq. +2-ABT	0 88	$Ni(NH_3)_6^{2+}$	1.09
Mn^{2+}aq	1.48	Mn^{2+}aq. +2-ABT	1 60	$Mn(NH_3)_n^{2+}$	1 65
Zn^{2+}aq.	0.99	Zn^{2+}aq. +2-ABT	1.22	$Zn(NH_3)_n^{2+}$	1 33

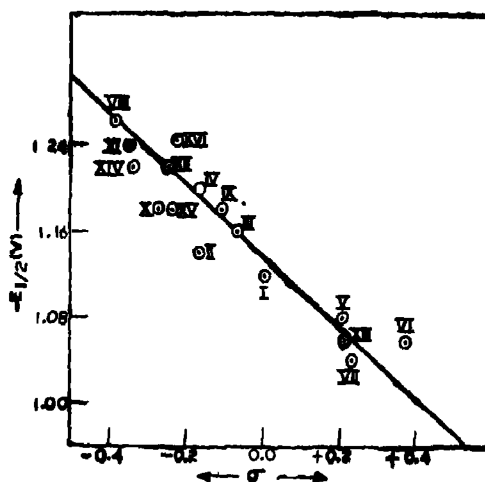


Fig 1. Plot of $-E_{1/2}$ vs σ for 2-aminobenzothiazoles in cobalt chloride.

Incidentally, these studies can provide a new approach to the reduction of difficultly reducible compounds.

Experimental

2-Aminobenzothiazoles having substituents in the benzene ring viz., H, 4-Cl, 5-Cl, 6-Cl, 4-CH_3, 5-CH_3, 6-CH_3, 4-OCH_3, 5-OCH_3, 6-OCH_3, 4-OC_2H_5, 6-OC_2H_5, 4-Br, 4,6-$(CH_3)_2$, 4,5-$(CH_3)_2$ and 5,6-$(CH_3)_2$ were synthesized by the method reported earlier[9]. The purity of the compounds was ascertained by repeated recrystallisation and tlc. Stock solutions (1.10×10^{-3} *M*) of the compounds were prepared in methanol (AnalaR). 0.01 *M* solutions of cobalt chloride, nickel chloride, zinc chloride, manganese chloride and aluminium chloride were pre-

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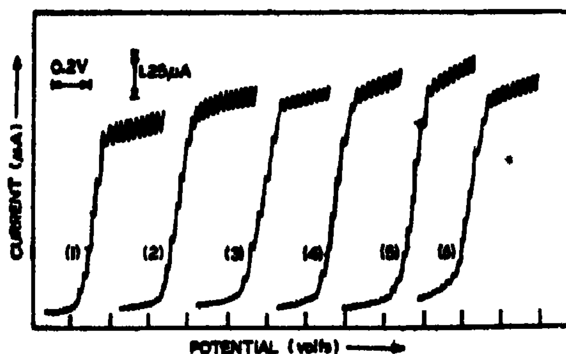
pared in doubly distilled water. The solutions used in these studies for recording the polarograms of the thiazoles were of the composition 0.1*M* NH_4Cl, 0.1*M* NH_3 and 0.001 *M* metal chlorides.

Apparatus and procedure : The polarographic curves were recorded on the Cambridge pen recording polarograph. The capillary characteristic was 1.27 mg 2/3 $S^{-\frac{1}{2}}$ in 1.0*M* KCl. A saturated calomel electrode was used as the reference electrode and the temperature was maintained at 30.0±0.1°. Inert atmosphere in the cell was kept by passing purified nitrogen gas for 10 min. *p*H measurements were made on the ELICO LI-10 *p*H meter.

Metal chlorides (1.0 ml), liq. NH_3 (1.0 ml), NH_4Cl (1.0 ml), water (6.0 ml) and 1.0 ml of the compound were mixed thoroughly with a stream of nitrogen. No maxima suppressor was used in the case of cobalt and nickel salts but the addition of 0.5 ml of 0.1% gelatin was found necessary in the case of manganese and zinc salts. For determining the value of 'n', the number of electrons involved in the reduction, the method of Devries and Kroon[10] was used using a mercury pool cathode. The temperature coefficient was determined by Nejedly's[11] method.

Results and Discussion

The polarograms of these compounds were recorded in various buffers in the *p*H range 2.0-12.0. No reduction wave was obtained. In the Brdicka solution a single well defined reduction wave was obtained (Fig 2). Similar waves were obtained when cobalt was replaced by other metal ions, viz., nickel, manganese, zinc and aluminium. Precipitation of the hydrous oxide took place with chromium and titanium salts and polarograms with these metal ions in ammonium chloride ammonia medium were not realized.



[Curves (1) a d (2) start at—0.9V, (3) starts at—0 8V, (4) and (5) starts at—0.6V and (6) starts at—1.16V]

Fig. 2. Some typical polarograms of 2-aminobenzothiazoles at concentration $1\times10^{-4}M$.
(1) R=H in $CoCl_2$; (2) R=6-CH_3 in $CoCl_2$; (3) R=4-Cl in $CoCl_2$; (4) R=H in $NiCl_2$; (5) R=5-Cl in $NiCl_2$; (6) R=H in $ZnCl_2$.

The polarographic behaviour of these compounds was entirely different from the usually reported behaviour in Brdicka solution in which a catalytic[12] wave is invariably obtained. On the other hand, the waves were found to be diffusion controlled. The irreversible nature of the waves was confirmed from log plots as well as from the shift in $E_{\frac{1}{2}}$ to more negative potential with the increase ($1.0\times10^{-4}M$ to $2.5\times10^{-4}M$) in concentration of the depolarizer[13]. The value of 'n', the number of electrons involved in the reduction at the d.m.e., was found to be two.

TABLE 2—POLAROGRAPHIC CHARACTERISTICS OF 2-AMINOBENZOTHIAZOLES IN BRDICKA SOLUTION

No.	R	$-E_{1/2}$, V	$\Delta E_{1/2}$, V	i_d/µA	αn	σ
1	H	1 12	—	4.95	0.48	0.00
2	4-CH_3	1 14	0 02	5.00	0.42	−0.17
3	5-CH_3	1 16	0.04	0.95	0.50	−0.07
4	6-CH_3	1 20	0 08	5.12	0 50	−0.17
5	4-Cl	1 08	0 04	5 25	0 48	+0.20
6	5-Cl	1 06	0 06	5.00	0.42	+0.37
7	6-Cl	1 04	0 08	5.10	0.42	+0.23
8	4-OCH_3	1 26	0 14	4 95	0.50	−0.39
9	5-OCH_3	1.18	0.06	5 10	0 48	−0.11
10	6-OCH_3	1 18	0 06	5 25	0.48	−0.27
11	4-OC_2H_5	1 24	0 12	5.00	0 42	−0.35
12	6-OC_2H_5	1 22	0 10	5 20	0 42	−0.25
13	4-Br	1 06	0 06	5 25	0 30	+0.21
14	4,6-$(CH_3)_2$	1 22	0 10	5 20	0 48	−0.34
15	4,5-$(CH_3)_2$	1.18	0.06	5.00	0.42	−0.24
16	5,6-$(CH_3)_2$	1 24	0 12	5 00	0.42	−0.24

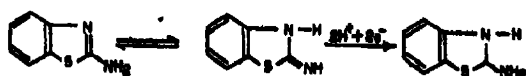
The half-wave potential of 2-aminobenzothiazoles in the presence of different metal ions in ammonium chloride ammonia solution are given in Table 3.

TABLE 3—HALF-WAVE POTENTIALS OF 2-ABT IN DIFFERENT METAL IONS

No.	R	$-E_{1/2}$, V			
		Co	Ni	Mn	Zn
1	H	1.12	0 88	1.60	1.22
2	4-CH_3	1 14	0 90	1.68	1.27
3	5-CH_3	1 16	0 93	1.68	1.30
4	6-CH_3	1 20	0 98	1.74	1 30
5	4-Cl	1.08	0.98	1 80	1 26
6	5-Cl	1 06	0 96	1.70	1.24
7.	6-Cl	1 04	0.94	1.68	1 25
8	4-OCH_3	1 26	0.98	1 56	1 28
9.	5-OCH_3	1.18	0 96	1.54	1.24
10	4-OC_2H_5	1 24	0.98	1.62	1.22
11	6-OC_2H_5	1.22	0 96	1 60	1.20
12	4-Br	1.06	0.94	1.76	1 20
13	4,6-$(CH_3)_2$	1.22	0.98	1.78	1.30
14.	4,5-$(CH_3)_2$	1 18	0 94	1 72	1.32
15.	5,6-$(CH_3)_2$	1 24	1.00	1.75	1.36

The 2-aminobenzothiazoles can exist in two tautomeric forms. Of these, the form having the −C=NH is polarographically active.

The reduction of these compounds, can, therefore, be represented as :



$CoCl_2$ being Lewis acid accepts a pair of electrons from the media viz., NH_4OH+NH_4Cl

which in turn attack the $-C{=}N-$ of 2-aminobenzothiazole (I) to form a donor acceptor complex (II) which is adsorbed at the mercury surface and orient itself on the surface in such a manner that a easily reducible moiety (III) is obtained.

$$H:\overset{H}{\underset{H}{N}}: + COCl_2 \longrightarrow H:\overset{H}{\underset{N}{N}}:\!\rightarrow \overset{Cl}{CO}Cl\ (M)^{\delta-}$$

(A base) (An acid)

$$-C{=}NH \xrightarrow{H^+} -\overset{|}{C}-NH_2 \xrightarrow{M^{\delta-}} -\overset{|}{C}-NH_2 \text{ (II)}$$

(I)

dissociation

$$-\overset{|}{\underset{H}{C}}-NH_2 + M \xleftarrow{2e+H^+} -\overset{|\delta+}{C}-NH_2 \text{ (III)}$$

The above view point was further confirmed by replacing cobalt chloride by other metal chlorides viz, nickel chloride, zinc chloride and manganese chloride which can act as a Lewis acid. In all these cases a similar 2e wave was observed (Table 3). An interesting point worth mentioning here was the different Lewis acid character of various metal ions. From Table 3 it is clear that order of capability of accepting a lone pair for various metal ions follows the order :

$$NiCl_2 > CoCl_2 > ZnCl_2 > MnCl_2$$

Effect of substituents : For studying the effect of substituents quantitatively, a sufficient number of derivatives were selected so as to cover a wide range of polar, steric and mesomeric effects of substituents. Since the values of the transfer coefficient and the mechanism of reduction for all the substituted aminobenzothiazoles were similar (αn=0.42 to 0.50 ; Table 2) the conditions for comparison of substituents quantitatively are fulfilled[14,15].

The values of half-wave potentials were correlated with Hammett total substituent constant (σ_α)[16]. The plots showing dependence of $E_{1/2}$ on σ are given in Fig 1. In all these cases not only the substituent *m*- and *p*- but the *ortho* derivatives showed a good correlation. In other reported series of compounds[15], *ortho* derivatives deviate from the $E_{1/2}$ vs σ plots due to steric hindrance. But in these compounds substituents are far away from the reduction site. Therefore, *ortho* derivatives could not sterically hinder the reduction of 2-aminobenzothiazoles. The value of specific reaction constant, ρ, was found to be 0.17 V, which is in good agreement with the value reported in the literature[17,18]. The positive value of ρ indicated a nucleophilic mechanism. In other words, the reduction of these compounds at d.m.e. involves electron uptake as the potential determining step.

Role of Lewis acids in the reduction of 2-aminobenzothiazoles : As these compounds undergo reduction only in the presence of Lewis acids, the role of Lewis acid in these electrode processes was elucidated. It appeared that a donor acceptor complex between 2-aminobenzothiazole (2-AB and metal plays a determinant role in the reduct of 2-aminobenzothiazoles at d.m.e. This comple adsorbed through diffusion at the mercury surf (and not simply by adsorption as evinced by non-existence of adsorption prewave) and orient it in such a manner that the hydrocarbon part the 2-ABT points towards the mercury surface the metal remains far away from the surface. T may be the possible reason for the non-appearai of the reduction wave of metals.

Although it is difficult to assign any defin reason for the non-reducibility of 2-ABT supporting electrolytes other than the Brdic solution, the possible explanation can be thou out in terms of inner sphere mechanism. Furt evidence of inner sphere mechanism for the red tion of these compounds was obtained by carry out studies in the presence of a surfactant. Si the electrode surface is negatively charged (E_m 0.62 V), the cationic soap, cetyltrimethylammoni bromide was used. The donor-acceptor comp

$$(-\overset{|}{C}-NH_2) \text{ would}$$
$$COCl_2$$
$$\uparrow$$
$$NH_3$$

have to compete with the surfactant for the s on the electrode surface, thereby increasing t energy of activation for the formation of t transition state $(-\overset{|}{C}-NH_2)$. This will

$$CO$$
$$\uparrow$$
$$NH_3$$

result in a lower rate of reduction.

Rate of reduction (K_{app}) for both inner a outer sphere reduction at the mercury electro surface is given by the equation[9,20] :

$$\log K_{app} = \log \frac{i}{FC_b}$$

where i is the current density at various appli potentials and C_b is concentration of the depolariz

The rate of reduction for 2-ABT in the absen and presence of surfactant is given in Table The plots of log K_{app} vs potentials E was line for a particular solution of constant concentrati of the depolarizer. The values of α_{app} can evaluted from the slope of plots of log K_{app} again -E which gives.

$$\alpha_{app} = -\frac{2.303RT}{F}\left(\frac{\log K_{app}}{\delta E}\right)$$

It is clear from Table 4 that the values of α_{a} are quite below 0.5 and K_{app} decreases in presen of surfactant. A very elegant proof of the reductic mechanism based on inner sphere path is th forthcoming on the basis of polarographic analys in the presence of surfactants.

TABLE 4—KINETIC DATA FOR ELECTRO REDUCTION IN BRDICKA SOLUTION

R	$-\log K_{app}$ (cms^{-1})*		$\Delta \log K_{app}$	α_{app}		$\left[\frac{\log K_{app}}{\log K_{app}, H}\right]$	ψ
	a	b	b-a	a	b		
H	0.266	0 289	0 023	0 019	0 016	1 00	0 96
4-CH_3	0.260	0 285	0 025	0 020	0 018	1 00	0 90
5-CH_3	0 260	0 289	0 029	0 019	0.96	1 26	0.96
6-CH_3	0.250	0 275	0 025	0 018	0 014	1 08	0 92
4-Cl	0.240	0 264	0 025	0 018	0 014	1 08	0 92
5-Cl	0.265	0 285	0 020	0 019	0 015	0 90	0 90
6-Cl	0.252	0.276	0 024	0 018	0 015	1 04	0.90
4-OCH_3	0.265	0 289	0 024	0 018	0 014	1 04	0 90
5-OCH_3	0 250	0 276	0 026	0 020	0 017	1 13	0 90
6-OCH_3	0 240	0 264	0 024	0 018	0 013	1 04	0 96
4-OC_2H_5	0 269	0 285	0 016	0 018	0 014	1 04	0 92
6-OC_2H_5	0.248	0 272	0 024	0 018	0 014	0 80	0 96
4-Br	0 245	0 264	0 019	0 018	0 013	1 04	0 92
4,6-$(CH_3)_2$	0 248	0 272	0 024	0 019	0 015	1 04	0 96
4,5-$(CH_3)_2$	0.258	0 285	0 027	0 018	0 014	1 17	0 96
5,6-$(CH_3)_2$	0 260	0 285	0 025	0 019	0 016	1 08	0 92

* a—in absence of surfactant, b—in presence of surfactant

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New Conceptions on the Equilibrium Properties of Electrolyte Solutions*

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The main flaw in Debye-Hückel theory of strong electrolyte solutions, which renders it untenable is pointed out. The concept of activity in liquid solutions is shown to be erroneous due to the supervening influence of cohesion. Internal pressure, being a measure of cohesive force in a solution, is suggested as a rational basis to understand the thermodynamics of electrolyte solutions.

A new model based on the postulation of statistically oriented solvent atmospheres around ions whose radii at a given temperature decrease with increasing concentration to reach a minimum at saturation has been proposed. These atmospheres act as mere dipoles due to fluctuations in their symmetry in addition to differences in the directions of orientation of water molecules around the cations and anions. Thus viewed, experimental studies of the internal pressure of an electrolyte solution at different concentrations gives a correlation with their physico-chemical behaviour.

THE problem of calculating the effect of electrostatic ionic interactions on the equilibrium properties of strong electrolyte solutions was solved explicitly by Debye and Hückel[1]. Soon after its formulation serious objections based on statistical mechanical arguments were raised by Fowler[2]. The validity of these objections was upheld by Frank and Thompson[3].

Defects of the Debye-Hückel theory: The main defects pointed out by the previous workers may be summarized as following :

1. The basic equation of Debye-Hückel theory was obtained by combining the Maxwell-Boltzman equation with the Poisson equation. This was considered unjustifiable as the potential of the Maxwell-Boltzmann equation is the potential of the average force whereas the potential of the Poisson equation is the average electrostatic potential[1,2].

2. The distribution function for ions in solution, used by Debye and Huckel, was criticised by Bagchi[4] who proposed other distribution functions.

3. According to the Debye-Hückel theory, the activity coefficient should continue to decrease with increasing concentration Experimental data for most salts show an initial decrease followed by a rise to high values[5]. This increase cannot be attributed to interionic attraction, but must be due to repulsion. Obviously any model which assumes only coulombic interactions cannot yield equations which will include the effects due to non-coulombic forces. In other words we cannot put into a model only coulombic forces and hope to derive equations which will cover non-coulombic effects as well.

The need, therefore, is for a theory which will formally recognise and accommodate non-coulombic forces. Devanathan[6] proposed a cell lattice model which fairly covered up the defects in Debye-Hückel theory but still has not stood the test of acceptability.

The main flaw in Debye-Huckel theory: The first postulate of the Debye-Hückel theory is that if the ions of an electrolyte lost their charges and became neutral particles, the solution would behave like a dilute solution obeying Henry's law. Ideal solutions are rare even in the field of non-aqueous, non-electrolyte solutions. An often quoted example is the system : ethylene bromide-propylene bromide[7]. But aqueous solutions of non-electrolytes can exhibit wide departures from ideality ; for example, the osmotic coefficient of an aqueous solution of sucrose is 1.508 at 6 m. This has been explained[8,9] by extensive hydration of the sucrose molecule ; the assumption that on the average each sucrose molecule removes 4.6 water molecules from the region of "free solvent" is sufficient to account for the osmotic coefficient upto at least 2 m. It has been shown[10] that the osmotic coefficient can be accounted for even upto saturation by assuming that there are eleven sites on the sucrose molecule each of which may be occupied by one water molecule. The osmotic coefficient of glycerol solutions can likewise be accounted for by postulating three hydration sites. This behaviour of non-electrolyte solutions is stressed because whatever their origin, the same effects should operate in electrolyte solutions, although modified by the charges on the ions.

In fact the total free energy of a solution can be written as,

$$G = G^{id} + G^{el} + G^{solv} + G^{E}$$

where G^{id} is the free energy of the ideal solution, G^{el} is the free energy resulting from interionic

*This paper is gratefully dedicated to my *Guru*, Professor N. R. Dhar, on the occasion of his 90th birthday.

forces of the Debye-Hückel type, G^{soly} is the free energy due to ion-solvent interaction and G^{E} is that due to ion-ion interactions apart from those of the Debye-Hückel type. If we go to solutions containing more than one electrolyte, their behaviour becomes complicated and interpretation more difficult.

In this background, if we can think of a measurable property of an electrolyte solution which can give a combined quantitative measure of the coulombic as well as the non-coulombic forces in terms of the properties of the constituent ions and the properties of the solvent molecules, the approach becomes more realistic.

When the solute is a gas and Henry's law is obeyed, the chemical potential of the solute in solution is given by the equation :

$$\mu_i = \mu_i^0 + RT\ln C_i$$

where C_i is the concentration, in gram-moles per litre of solution and μ_i^0 is the chemical potential of one mole of the solute in a solution of unit concentration.

We know that Henry's law[11] is inapplicable to solutions of non-electrolytes and electrolytes, more so at higher concentrations. It is also apparent that RT in the above equation has its origin in ideal gases. The non-ideality of real gases is due to the intermolecular forces of attraction. What distinguishes a liquid from a gas is the enormous cohesion in the former which can be measured by the internal pressure, $\left(\frac{\partial U}{\partial V}\right)_T$, where U is the internal energy and V the volume of the system. If we have a relation between the forces of cohesion, namely, the internal pressure of a liquid system and the vapour pressure above it, we have a good start.

A new approach : In this background the very idea of the chemical potential of a solute in a liquid solution being directly made proportional to RTlna is ill-founded. Further, in an electrolyte solution to relate the activity co-efficient solely to the interionic forces is erroneous. The activity coefficient, if at all, should reflect simply the degree of cohesion in a solution system rather qualitatively.

Recently Srinivasan, Savariraj and Suryanarayana[13] derived from statistical thermodynamical considerations, the relation between the vapour pressure P and internal pressure π_i.

$$P = P_c \exp. [-\pi V/2 RT]$$

where P_c is the critical pressure, R the gas constant and T the absolute temperature. This has been tested for 30 polar and non-polar liquids. Suryanarayana[13] applied the above equation to electrolyte solutions and brought out the fundamental importance of internal pressure in relation to Raoult's law, osmotic pressure, osmotic and activity coefficients of electrolyte solutions.

Dack[14] and Suryanarayana [15] have analysed the significance and usefulness of internal pressure in liquid systems. The first review on this subject was by Richards[16]. Later Hildebrand and Scott[17] and Haward and Parker[18] discussed the importance of internal pressure in liquids.

Suryanarayana[19] recently emphasised that whatever may be the liquid system, a solvent, a mixture of solvents or a solution either of a non-electrolyte or an electrolyte, its state is thermodynamically defined by the internal pressure, the free volume and temperature.

Internal pressure reflects the sum-total of solvent-solute, solute-solute and solvent-solvent interactions in a liquid solution system. However, one has to evolve a credible method of quantitatively measuring internal pressure, particularly in an electrolyte system wherein we have all kinds of interactions.

Measurement of internal pressure : A general method of measuring internal pressure is based on the thermodynamic equation of state,

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T$$

The first term on the right hand side is the product of temperature and the temperature coefficient of pressure and the second term is the internal pressure. For liquid solutions P is very negligible compared to the internal pressure. Hence the first term is almost equal to the second term. Hence one way of measuring internal pressure is to compute it via the temperature coefficient of pressure. For instance, Lee and Hyne[20] report internal pressure values of potassium chloride solutions at different concentrations and at increasing temperatures. In both, the trend is one of increase. Similarly for water, this method yields an increase of internal pressure with increase in temperature. This is rather anomalous as we know that with increase in temperature the surface tension of liquids decreases. Suryanarayana[21] showed a quantitative relation between surface tension and internal pressure in liquid systems. Suryanarayana[19] showed alternatively a new method of measuring internal pressure instead of via the temperature coefficient of pressure. This method involves measurements of ultrasonic velocity, viscosity and density of solutions. The anomalous results of the measurements of internal pressure by Lee and Hyne[20] can probably be due to the thermodynamic temperature coefficient of pressure, namely, $\left(\frac{\partial P}{\partial T}\right)_V$ or α/β_T being unconsciously based on gas thermodynamics. Measurements of $\left(\frac{\partial U}{\partial V}\right)_T$ by the method of Suryanarayana[19] gives the expected trend of a fall in internal pressure with increasing temperature as it is based on the properties of condensed systems[19,21].

Suryanarayana and Kuppusami[22] reported the internal pressure and free volume for electrolyte solutions of NaCl, KCl, $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4, $ZnSO_4$, $CuSO_4$, KI, $Pb(NO_3)_2$, tetramethyl ammonium chloride and one non-electrolyte, glucose, in a wide range of concentrations including saturation. A general quadratic relation has been

observed between the molality on the one hand and the internal pressure and the free volume on the other hand :

$$\pi_i = \pi_0 + Am^2 + Bm$$
$$V_f = V_f o + Cm^2 + Dm$$

π_i and V_f are for the solutions and π_0 and $V_f o$ are for the solvent. A, B, C and D are dependent on temperature. For all the solutions, at every concentration, the variation of either the internal pressure of the free volume with temperature can be expressed as,

$$\pi_i(T) = a.\exp.(-bT)$$
$$V_f(T) = c.\exp.(gT)$$

where a, b, c and g are constants depending on concentration of the electrolyte and are yet to be rationalised. Glucose solutions and also pure water show the above quantitative relations.

By far the best treatment which emphasises the solvation of the ions in discussing the activity coefficients is that of Robinson and Stokes[23]. But even their equation gives agreement with experimental results only upto about $2m$ solutions, above which it fails We [22] have found that the following equation expresses quantitatively the relation between the activity coefficient and internal pressure of the medium applicable to NaCl, KCl, NH_4NO_3 solutions

$$\gamma = a\left(\frac{\pi_i}{\pi_0}\right) + b\left(\frac{\pi_i}{\pi_0}\right)^{\frac{1}{2}} + C$$

where a, b and c are empirical constants to be rationalised by further studies The calculated and experimental values agree remarkably upto the highest concentration. This definitely means that activity coefficients have their origin in the differences in the degree of cohesion of different electrolyte solutions at different concentrations. Thus the behaviour of solutions in general is conditioned by their internal pressures and free volumes at a given temperature. In the case of electrolyte solutions, as with non-electrolyte solutions, the non-coulombic forces in terms of cohesive forces play a far greater role Ion-dipole and dipole-dipole interactions assume a major role Of these contributions, those arising from the interactions of the ion-solvent complexes are of greater significance

A new model : When an electrolyte is dissolved in water, the important event that occurs is hydration. Friedman and Krishnan[24] gave a comprehensive review of the thermodynamics of ionic hydration. Frank and Wen-Yang Wen[25], Samoilov[26] and Gurney[27] made significant contributions to a rigorous understanding of what happens to water molecules around an ion. These advances point to the existence of primary hydration sheath in which region the solvent molecules are immobilized due to intense electrostriction. Surrounding this envelope is the region of structure breaking, and beyond this is the region of structurally normal solvent The intermediate region is referred to as the secondary hydration sheath. The secondary water envelope can exchange water molecules rapidly with structurally normal water, the frequency being of the order of 10^9. Samoilov[26] showed that the value of the energy of activation for this exchange is very much less than the hydration energy.

Coming on to the new model, ions — both positive and negative — have radially orienting electric fields. In this orienting field, the solvent molecules get appropriately aligned[28] parallel to the electrostatic field generated by the positive or negative ions resulting in a minimum potential energy. Beyond the primary hydration limit also, one may have to think in terms of an atmosphere of solvent molecules around the ions having statistically a spherical symmetry. We may call this statistically oriented solvent atmosphere. The radius of this atmosphere should be a function of temperature, concentration of the electrolyte and specifically the surface density of the charge on the ions — positive or negative. Thus the statistically oriented solvent atmosphere either for a cation or for an anion should effectively behave with interactions as between dipoles. It must be clear that any disturbance in the thermodynamic equilibrium state of the system should perturb these atmospheres and disturb the overall entropy of the system. Once this picture is accepted, then follows the same usual way of looking at an electrolyte solution as we do at a pure liquid or a non-electrolyte solution In other words, as Pitzer[29] rightly pointed out, a really satisfactory general theory of non-electrolytes could be transferred to the concentrated electrolyte problem

The radius of the statistically oriented sol ent atmosphere naturally goes on diminishing as the concentration tends to increase towards saturation. One should imagine that at saturation concentration a minimum radius of the statistically oriented solvent atmosphere is obtained. What requires to be looked at in this model is the balance between attractive and repulsive forces in the solutions due to statistically oriented solvent atmospheres. By very definition and its nature, internal pressure of a solution is a balance between the attractive and repulsive forces. However, in the equations given by Suryanarayana and Kuppusami[22] relating to internal pressure of a solution either to the concentration or to the activity coefficient, the constants involved in the quadratic equations are such that the one belonging to the higher power term relates to attractive forces and the other relating to the lower power term to the repulsive forces. In other words, a rationalised theory of solutions which can be common both for non-electrolyte and electrolyte solutions consists in working out attractive and repulsive forces quantitatively based on the overall internal pressure of a solution. This model makes the ions, taken together with the statistically oriented solvent atmospheres, similar to floating dipoles contributing to the overall cohesion of the solution. They may be taken as dipoles because the spherical symmetry should be expected to be perturbed due

to random fluctuations. The solvent atmosphere, if spherically symmetrical, should mean neutral spheres in the case of both cationic and anionic atmospheres. For cohesion to exist, dispersion forces are a minimum necessity. Hence in a fluctuating situation, the spherical symmetry is perturbed statistically and gives rise to dispersion forces. Even otherwise, due to the differences in the directions of orientation of solvent molecules around the cations and anions taken together with the fluctuations in the symmetry of the oriented solvent atmospheres, dipolar type of interactions should be expected between the floating oriented atmospheres.

It is often said that Passinsky's method[30] yields ionic hydration values which are too high at lower concentrations and fall off reaching a limit as one approaches saturation. This is an indirect evidence of the existence of statistically oriented solvent atmospheres around an ion neutralising the central ionic charge.

In this background one should imagine that at saturation concentration not only the radius of the statistically oriented solvent atmospheres should be the minimum but also the potential energy due to this arrangement should be the minimum compared to other lower concentrations. One can not think of free solvent molecules not forming a part of these spheres of atmospheres. Bencowitz[31] found empirically that by using the ratio of any molality of an electrolyte solution to that at saturation, which he called the "degree of saturation", instead of the molal concentration, vapour pressure lowerings even at high concentrations were explained by simpler relationships Suryanarayana and Venkatesan found similar relationships[32-34] with viscosity and conductance in electrolyte solutions. Suryanarayana[35] made an analysis of these ideas connected with saturation concentration and suggested the term concentration potential for the degree of saturation. From Suryanarayana's[35] analysis, it looks that the concentration dependent physical properties of electrolyte solutions are quantitatively related to the size of these statistically oriented solvent atmospheres. Further, the variation in any physical property with concentration is expressed in a simpler quantitative way when the ratio between the size of the solvent atmosphere at a given concentration to that at saturation is considered. The size of the solvent atmosphere seems to be conditioned by the overall attractive and repulsive forces as a result of the sum-total of 1-2, 2-2 and 1-1 interactions. At a given concentration the sizes of the cationic and anionic solvent atmospheres need not be the same. But their variation with concentration follows simpler laws when one takes their ratio with those at saturation. Internal pressure being a measurable property should be able to explain the behaviour of mixed electrolyte solutions also.

A further evidence of the role of statistically oriented solvent atmospheres is that at a given concentration of an electrolyte solution even upto saturation concentration, Suryanarayana and Kuppusami[22] reported that the variation of equivalent conductance with temperature is such that,

$$\Lambda_0 (T) = h - g \cdot \pi_i (T)$$

where equivalent conductance virtually varies with internal pressure at the respective temperature, h and g being constants. One should expect that an increase in temperature will have a disorienting influence on the solvent atmosphere due to thermal fluctuations introducing more randomness and lowering the internal pressure particularly due to the inter-solvent atmosphere forces becoming lesser

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Action of Electrolytes on Lyophobic Sols

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Dhar and coworkers showed that besides the valency of the oppositely charged ion of the electrolyte its precipitation value for a lyophobic sol is defined by the specific adsorption of similarly and oppositely charged ions by the colloid particles, dilution of the sol, and also on the mode of addition of electrolytes, in parts or all at once.

The precipitation value is affected by the time 't' the electrolyte is in contact with the sol. It is also affected by temperature. Ghosh and coworkers showed the applicability of the rate equation for a chemical reaction to coagulation process, so that $\frac{1}{t} = kpz \exp(-E/RT)$, where $\frac{1}{t}$ is proportional to the rate of coagulation, p is the probability of formation of a stable aggregate, E the energy of activation, and z is number of collisions in unit time. In this paper further experimental support has been obtained by the study of gelation as well as coagulation of ferric and aluminium phosphate sols effected by electrolytes at different temperatures It has been also shown that $\log kpz = \alpha \log C + \beta$, where C is the concentration of the electrolyte, α and β are constants, and therefore $\log t = \alpha \log C + k_1$, where k_1 is constant provided E does not vary for different concentrations of the electrolyte. This relation of the time of coagulation and concentration of the coagulating electrolyte is very similar to those proposed by several other workers.

It is suggested here that p and E define the stability of the sol. E is large if (i) attractive force of the aggregating particle is small and (ii) the electric charge, which repel the particles to come together is large, whereas p increases with the decreasing electric charge on colloid particles effected by an electrolyte. It has been repeatedly observed that where E is large, kpz or p is also large, and such behaviour is so common for chemical reactions.

The sols of the phosphates of ferric and aluminium become unstable by adding dioxan, which lowers the dielectric constant of the medium and compresses the double layer, a behaviour similar to the initial condition produced by a coagulating electrolyte. But considerable lowering of energy of activation suggests that dioxan also increases the attractive force of the colloid particles of the two phosphate sols investigated here.

COLLOIDAL systems are thermodynamically unstable. The finely dispersed particles expose large surface area and therefore possess large free surface energy, which tends to decrease by their aggregation. The two recognised factors which check it are (i) electrical repulsion of the charged particles, and (ii) decrease of the free surface energy by such process as high solvation of colloid particles as in the case of lyophilic sols.

Action of electrolytes on lyophobic sols is to decrease the charge on the dispersed particles and thus render them unstable. Investigations from very early times led to such generalisations as Schulze-Hardy law and Whetham's rule for the precipitation values of different electrolytes. In a number of publications Ghosh and Dhar[1] showed that besides the valency of the oppositely charged ion, the specific adsorption of both similarly and oppositely charged ions, dilution of the sol, and even the mode of addition of the electrolyte (such as in parts or all at once) define its precipitation value. The phenomenon of positive acclimatization occurs because of the adsorption of similarly charged ions, whilst specific adsorption of the oppositely charged ions leads to negative acclimatization, first reported by Ghosh and Dhar. Levine and Bell[2] also pointed out that variation in Schulze-Hardy law occurs due to specific adsorption of oppositely charged ions.

Whetham deduced that the precipitation values P_1, P_2, P_3 for mono-, bi-, and trivalent coagulating ions of an electrolyte bear a simple relation such that

$P_1 : P_2 : P_3 = 1 : x : x^2$, where x is less than unity. This relation is hardly found to be true.

Chakravarti, Ghosh and Dhar[3] pointed out that the double layer surrounding the colloidal particle acts as a barrier for the approach of the oppositely charged ions to the colloid particle to neutralise its electric charge. Working on such assumption they modified Whetham's rule as

$P_1 : P_2 : P_3 = 1 : \frac{1}{2}\alpha : \frac{1}{3}\alpha^2$ ... ... (i) and $\alpha = \exp\left(\frac{-Qe}{DrkT}\right)$, where Q is the charge on the colloid particle, e the electronic charge, D the dielectric constant, r the effective distance of the double layer, k the Boltzmann constant and T the

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absolute temperature. α is a proper fraction and tends to be unity when Q or the electric charge on the colloid particle is very small. In such a limiting case

$P_1 : P_2 : P_3 = 1 : \frac{1}{2} : \frac{1}{3}$ ... ... (ii), later Verwey and Oberbeek[4] considered the interaction of the double layers of two colliding charged dispersed units and have shown

$P_1 : P_2 : P_3 = 1 : (\frac{1}{2})^6 : (\frac{1}{3})^6$ .. . (iii), when the colloidal particles are charged The relation (iii) becomes

$P_1 : P_2 : P_3 = 1 : (\frac{1}{2})^2 : (\frac{1}{3})^2$ (iv), when the charge on the particles is removed.

Gore and Dhar[5] dialysed a positively charged sol of ferric hydroxide to different extents and noted that as the purity of the sol is increased the precipitation values P_1, P_2, P_3 for chloride, sulphate and ferricyanide ions approach each other. Similar results were obtained by Ghosh and Rathi[6] for ferric and aluminium phosphate sols, but they were unable to verify any of the relation (i) and (ii) or (iii) and (iv). It is necessary to state here that the relations have not taken into account the specific effect of the ions of the coagulating electrolytes on the dispersed particles, and therefore applicability of the equations derived by Dhar and Ghosh or Verwey and Overbeek cannot be expected to be true for different electrolytes.

Solvation and stability: High solvation of colloid particles as those of lyophilic sols renders them stable towards moderate concentrations of electrolytes. Most of the biocolloids such as gelatin, staroh, belong to this group. However, there are a number of inorganic compounds, which yield viscous sols and their dispersed particles are highly solvated and easily yield gels by the action of electrolytes, and the gelation values for different electrolytes more or less follow Schulze-Hardy law[7]. Prakash and Dhar[8] prepared gels of such inorganic compounds and studied their thixotropy and syneresis. It is suggested that such sols have highly solvated dispersed units but have some bare spots which join up on charge neutralisation entraining the solvent The forces of binding are sufficiently loose so that the gel formed shows thixotropy and syneresis on ageing. Hauser[9] made an ultramicroscopic study of the thixotropic behaviour of a highly solvated suspension of bentonite and observed that the suspended particles gradually lose Brownian movement and take up position though there is no material contact. Their movement can be easily revived by shaking. Banerji and Ghosh[10] made rheological study of a viscous gel yielding sol of ferric phosphate and showed the plastic behaviour of the sol indicating the existence of a structure even in the so called fluid state. This shows that a loose structure is present in this sol.

Effect of non-electrolytes: The stability of sols towards an electrolyte has been largely investigated. Obviously a non-electrolyte cannot neutralise the charge on the colloid particles, but can well affect the electrical interactions of the charged particles by varying the dielectric constant of the medium. If the lowering of dielectric constant decreases the thickness of the double layer, the effect is similar to that produced by the addition of an electrolyte to coagulate a sol. Freundlich[12] suggested that lowering of dielectric constant leads to decrease of the electric charge on the colloid particle and thus decreases the precipitation value of an electrolyte. Keesom[13] reported that the solutes, urea and glycol, increase the dielectric constant of water and render a sol of arsenious sulphide stable towards electrolytes. Mukherji, Raichoudhuri and Rao[18] reported from the cataphoretic study of arsenious sulphide sol, that the mobility of colloid particles continuously decreases in an electrical field by the addition of a few non-electrolyte increasing or decreasing the dielectric constant of water Prasad and Ghosh[11] showed that glucose, which tends to decrease the dielectric constant, stabilises several hydroxide sols Nand and Ghosh[14a] observed that ferric hydroxide sol becomes unstable in the presence of dioxan, which remarkably lowers the dielectric constant of water. Yadav and Varma[15] found that the sols of chromium and aluminium hydroxides become unstable in the presence of formamide, which increases the dielectric constant of water. It thus appears that factors other than the effect of the non-electrolyte on the dielectric constant are involved, which make a sol stable or unstable towards an electrolyte.

Equally a large amount of literature is available on the effect of non capillary and capillary active non-electrolytes on the stability of sols, but no general conclusion can be drawn from such results. Weiser[16] therefore concluded that several factors describe the effect of a non-electrolyte on the stability of a sol These are (i) dielectric constant of the medium, (ii) the viscosity, (iii) effect on ion activity and (iv) effect on the adsorption of ions of the coagulating electrolyte. It is necessary to mention here that a non-eletrolyte effecting the free surface energy of the dispersed phase is also important for the stability of a sol.

Effect of time on precipitation value: Precipitation value of an electrolyte for a sol decreases with the increase in time of its contact with the sol. Several equations have been suggested from time to time to relate time of contact, 't', with the concentration of the electrolyte, C, added to coagulate the sol. Paine[17] suggested the relation $-\log t = k_1 \log C + k_2$...(1) where k_1 and k_2 are constants and are similar to those of Mathews and Murphy[18] viz., $1/t = aC^n$, where a and n are constants.

von Smoluchowski[19] considered that after the charge neutralisation of the colloid particles by an electrolyte, they combine when they are within the range of attraction, R, effected by diffusion process determined by the coefficient D so that,

$\Sigma n = \frac{n_o}{1 + 4\pi DRn_o t}$, where Σn is the number of particles of all stages of aggregation left over after time 't' out of the total number of particles n_o in the initial stage. It is assumed that DR remains

constant so that $4\pi DRn_0$ is constant and denoted by $\frac{1}{T}$. Smoluchowski further considered that during slow coagulation, the charge neutralisation on colloid particles is not complete and hence

$\Sigma n = \frac{n_0}{1+\epsilon\frac{t}{T}}$ ... (2), where ϵ is less than unity.

Ultramicroscopic investigations of Zsigmondy[20], and also of Westgren and Reitstotter[21] for the aggregation of particles of a gold sol by an electrolyte, and of Kruyt and van Arkel[22] for that of a selenium sol show that the relation (2) is not applicable for ϵ continuously decreases and that the aggregation of coarser particles becomes so slow as if no further growth will occur.

Mukherji and Papaconstantinoa[23], and later Rai and Ghosh[24] and also Ghosh[25] used spectrophotometric method to study aggregation of colloid particles and showed that ϵ continuously decreases as the aggregation proceeds. Ghosh[26] pointed out that DR should progressively decrease as R cannot increase with the progress of aggregation as to compensate the decrease of D, so that DR remains constant With increasing aggregation, the surface area and therefore surface energy per unit area continuously decreases.

Ghosh and coworkers[27] found that decrease of ϵ occurs with increasing time so that $\epsilon = \frac{k}{1+\alpha t}$. where k and α are constants. Thus they modify the relation (2) as

$\frac{\Sigma n}{n_0} = \frac{1+at}{1+bt}$. (3), where a and b are constants and $b>a$.

The above relation (3) is reported to be applicable for the coagulation of several sols, and thus proves the contention of Ghosh[26] that DR continuously decreases as R does not increase proportionately as more and more aggregated particles appear in the system

It is well known that the time for complete coagulation decreases with increasing concentration of the coagulating electrolyte, and that beyond a certain concentration, the coagulation time t_r is more or less constant. This is the region of rapid coagulation and Reernik and Overbeeck[28] defined the retarding or stability factor W as the ratio t_s/t_r, where t_s is the time for slow coagulation. Basing their calculations for the interacting particles with energy barrier arising out of the electric charge, they obtain the relation,

$\log W = -k_1 \log C + k_2$ ..(4), where k_1 and k_2 are constants. Since t_r is practically constant, equation (4) is similar to that of Paine. The plots of log W vs log C give a straight line, which gradually bends as t_s approaches t_r and finally runs parallel to log C axis, when W becomes unity.

An equation relating W with the concentration of the added electrolyte was proposed by Packter[29] viz.,

$\log W = C_1\gamma^4 - C_2\gamma^2\sqrt{C_e}$ (5), where C_1 and C_2 are constants, C_e is the concentration of electrolyte added, and γ is defined by $\frac{\exp(Ze\Psi/2kt)-1}{\exp(Ze\Psi/2kt)+1}$ where Z is the valency of the coagulating ion, e the electronic charge, Ψ the surface potential, k the Boltzmann constant and T the absolute temperature. The relation (5) is based on the theory of stability of sols and assumes that (i) for low concentration of the electrolyte only the double layer is compressed and (ii) that γ does not change when coagulation occurs.

Bhattacharya and Bhattacharya[30] proposed more or less an empirical relation $\frac{1}{c-a} = \frac{n}{m}t + \frac{1}{m}$...(6), where c is the concentration of the electrolyte added for coagulating the sol in time t, 'a' the concentration of the electrolyte coagulating the sol in infinite time and n and m are constants.

Ghosh[31] deduced the above relation from the considerations of Verwey and Overbeek. The relation, however, is true for limited range of the concentration of the coagulating electrolyte[32].

Effect of temperature on the stability of a sol: This was investigated by Lach and Goldbury[33], who found the time of coagulation, t, of a gold sol by an electrolyte proportional to η/T where η is the viscosity of the medium water Similarly, Bose and Freundlich[34] found the applicability of a similar relationship for the slow coagulation of cupric oxide sol. Hurd and Latterson[35] investigated the effect of temperature for the gelation of silicic acid sol. Ghosh[36] also determined the effect of temperature of the same sol at different pH. Ghosh and co-workers[37] also studied the effect of temperature on the coagulation of some sols as well as the gelation of ferric succinate sol All these investigations find that at higher temperature the sols become more unstable.

It is necessary to recall the concept of Reerink and Overbeek that coagulation is a bimolecular process specially in the initial stages, so that $-\frac{dn}{dt} = KN^2$, where N is the number of particles present initially, n is the number of primary particles taking part in the aggregation process and K is a constant, which varies with temperature i.e., $K = K_0 \exp\left(-\frac{E}{RT}\right)$, where E is the energy of activation or the energy necessary to overcome the repulsive force due to electric charge. Verwey and Overbeek[38] related the stability factor W with the energy of activation as $\frac{1}{W} = \exp\left(-\frac{E}{RT}\right)$, so that when large concentration of an electrolyte is added, the coagulation becomes rapid where W is unity and therefore the heat of activation reduces to zero.

Ghosh[39] considers the aggregation process very similar to a chemical reaction as both the processes

occur through collision of particles. Aggregation of colloidal units first start with primary ones, and the newly formed unit can further grow by collision with primary or aggregated ones. This process continues till the aggregate becomes sufficiently large to lose its Brownian movement resulting in coagulation. Furthermore, the colliding particles first form an 'activated aggregate' by the collision of the two particles of requisite activation energy and the formation of the lasting aggregated units depends upon the probability factor p. If t is the time taken for complete coagulation of a definite amount of sol by the presence of an electrolyte and the rate taken as proportional to $\frac{1}{t}$, Ghosh and co-workers[40] suggest the relation

$$\frac{1}{t} = kpz \exp\left(-\frac{E}{RT}\right) \quad \ldots (7)$$

$$\text{or } \log t = -\log kpz + \frac{E}{2.3RT} \quad \ldots (8)$$

(a relation similar to a chemical process) where k is a constant, z the number of collision in unit time and T the absolute temperature. From the above relation it is seen that the stability of a sol depends on the values of p and Ghosh and co-workers[40] found the applicability of the relation (8) in as much as the plots of log t vs $\frac{1}{T}$ for a concentration of the coagulation electrolyte gave a straight line for the coagulation of some sols investigated by them earlier.

In this paper we have examined the applicability of the equation (8) for the gelation time for a ferric phosphate sol effected by an electrolyte at three stages of dialysis and also the sol of aluminium phosphate, which at its first and second stages of dialysis yields a bulky coagulum with an electrolyte but at its third stage gave a hazy gel.

Experimental

Ferric phosphate sol was prepared by the interaction of 1.0 l of 0.5 *M* $FeCl_3$ solution with 0.5 l of *M* KH_2PO_4. The sol so obtained was yellowish which on dialysis in a cellophane bag gradually became red. The analysis of the sol showed that gradually a basic iron phosphate or a mixture of $Fe(OH)_3$ and $FePO_4$ appeared with prolonged dialysis. These samples of the sols at different stages of dialysis were withdrawn and diluted with water so that the iron content of the three sols was the same i.e., 5.8 g of Fe per l. The three sols were designated as A_1, A_2 and A_3 and the *p*H of these were 2.7, 3.1 and 3.4, respectively. With further dialysis of the sol, the *p*H increased to 3.6 and formed a gel in the cellophane bag itself.

Aluminium phosphate sol was prepared by the interaction of 600 ml of 1.0 *M* aluminium chloride and 500 ml of 1.0 *M* of diammonium hydrogen phosphate solutions leaving some aluminium chloride in excess. The sol was diluted to 1500 ml and dialysed in a cellophane bag. Three samples of the sol were withdrawn at different stages of dialysis and diluted to contain 1.8 g of Al per l. The sols B_1, B_2 and B_3 were at *p*H 3.0, 3.4, 3.8 respectively. When coagulated by an electrolyte sols B_1 and B_2 yielded heavy coagula, whilst sol B_3 gave a hazy gel.

Method adopted to measure the gelation or coagulation time : Various optical methods are used to measure coagulation time of sols, but the formation of a transparent gel cannot be easily noted by any of them. There is hardly any change in the optical density when the sol sets to a gel, specially when the gelation process is slow. Hence gelation time is recorded by the observation that the gel formed does not flow out in a test tube of uniform diameter of 1.5 cm and 12.5 cm in length. The recorded time of gelation is the mean of three observations. In the case of coagulation of the sols B_1 and B_2, the time was noted by the separation of the coagulum at the top layer in the test tube. It should be noted that the variation was within 2.5% when the time of observation was over 200 min, and it slightly decreased for smaller time. In Table 1, the observations for the gelation of sol A_1 by different concentrations of K_2SO_4 are recorded in the absence and also in the presence of the non-electrolyte dioxan, which decreases the dielectric constant of water remarkably and is sufficiently inert. The experiments have been carried out at four different temperatures in a thermostat.

To verify the applicability of relation (8) log t vs $\frac{1}{T}$ are plotted, and it will be seen that they yield straight lines for each concentration C of the electrolyte (see Fig. 1). From the inclination of the line the value of E can be obtained, and the value of log kpz can be calculated. These values of E and log kpz for different concentrations of electrolyte are given in Table 2. In a similar way the values of log kpz and E have been calculated when the gelation takes place in the presence of dioxan, and are also noted in Table 2.

As described above the values of E and log kpz have also been determined for the gelation of ferric

TABLE 1—GELATION OF FERRIC PHOSPHATE SOL A_1 BY POTASSIUM SULPHATE

Gelation value, in m moles/litre ×10	Time of gelation in min at 30°	35°	40°	45°	Time of gelation in min in 10% dioxan at 30°	35°	40°	45°
8.0	580	270	132	65.5	210	135	85	54.5
8.8	435	192	95	45	140	85	55	33.2
9.6	310	135	65.5	30.5	90.5	55	35.2	21.0
10.4	178	80	35	17 5	50	30.5	17.5	10.2
11.2	110	45	21	9.5	30.5	20.2	8.2	4.5
12.8	68	25	10.5	—	—	—	—	—
16.0	47	16	7	—	—	—	—	—

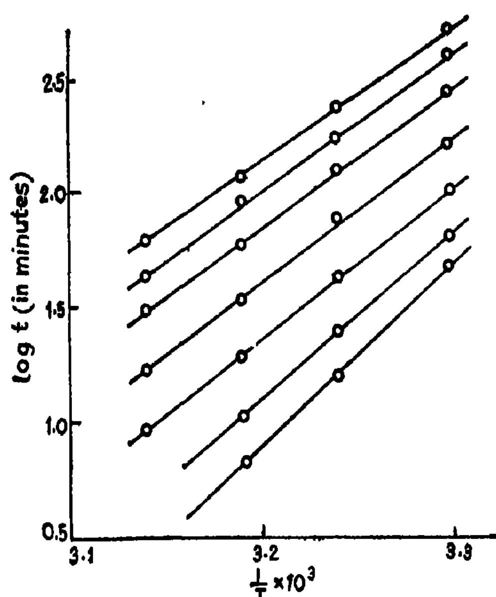


Fig. 1

phosphate sols A_2 and A_3, and also for the coagulation of aluminium phosphate sols B_1 and B_2, as well as for the gelation of highly dialysed aluminium phosphate sol B_3. All these values are given in Tables 3 to 7.

A perusal of Tables 2 to 7 shows that the values of log kpz and therefore p increase with the increasing concentrations of the electrolyte potassium sulphate, added for gelation or coagulation. It will be seen that the plots of log kpz vs log C yield straight lines (see Fig. 2) so that

$\log kpz = \alpha \log C + \beta$. (9), where α and β are constants. Hence the relation (8) becomes

$\log t = -\alpha \log C - \beta + E/2.3\ RT$, and if activation energy E does not vary, we have

$\log t = -\alpha \log C + k$, ... (10), which is very similar to those of Paine or Verwey and Overbeek relating the time of coagulation with the concentration of the coagulating electrolyte.

Ghosh and Roychowdhury[41] have suggested

Table 2—Gelation of Ferric Phosphate Sol A_1 by Potassium Sulphate

Temperature range 30°–45°

log C×10	0.9031	0.9445	0.9823	1.0170	1.0492	1.1072	1.2041
			In aqueous medium				
log kpz	17.86	18.82	19.72	20.83	21.48	23.62	26.46
E in K cals	29.0	30.0	30.4	32.0	32.6	36.8	39.2
			In 10% dioxan solution				
log kpz	10.85	11.46	12.05	12.72	16.27	–	–
E in K cals	18.4	19.0	19.6	20.2	24.8	–	–

Table 3—Ferric Phosphate Sol A_2, Electrolyte for Gelation : Potassium Sulphate

Temperature range 30°–45°

log C×10	0.6812	0.7160	0.7482	0.7782	0.8062	0.8573	0.9031	0.9445
			In aqueous medium					
log kpz	18.62	19.62	20.60	21.15	21.80	22.80	24.23	24.81
E in K cals	29.9	31.1	32.2	32.8	33.4	34.5	36.4	36.9
			In 10% dioxan solution					
log kpz	12.57	13.14	13.77	14.42	–	–	–	–
E in K cals	20.7	21.3	21.9	22.5	–	–	–	–

Table 4—Ferric Phosphate Sol A_3, Electrolyte for Gelation Potassium Sulphate

Temperature range 30°–45°

log C×10	0.2041	0.2553	0.3010	0.3424	0.3802	0.4472	0.5315	0.6433
			In aqueous medium					
log kpz	19.00	20.08	21.13	21.76	22.46	24.05	25.93	28.20
E in K cals	30.5	31.7	32.8	33.4	34.0	35.7	38.0	40.9
			In 10% dioxan solution					
log kpz	13.82	14.89	15.56	16.27	–	–	–	–
E in K cals	22.5	23.6	24.2	24.8	–	–	–	–

Table 5—Aluminium Phosphate Sol B_1, Electrolyte for Coagulation . Potassium Sulphate

Temperature range 30°–45°

log C×10	2.2041	2.5553	2.3010	2.3424	2.3802	2.4150	2.4472	2.4771	2.5315
			In aqueous medium						
log kpz	12.16	13.11	13.60	14.15	14.70	15.70	17.01	18.77	20.99
E in K cals	20.7	20.4	22.5	23.0	23.6	24.8	26.5	28.80	31.7
			In 10% dioxan solution						
log kpz	7.95	8.91	9.89	11.25	12.07	14.05	15.84	17.25	–
E in K cals	14.4	15.5	16.7	18.4	20.7	21.9	24.2	25.9	–

TABLE 6—ALUMINIUM PHOSPHATE SOL B_2, ELECTROLYTE FOR COAGULATION : POTASSIUM SULPHATE

			Temperature range 30°–45°						
log C × 10	1.3424	1.380	1.4150	1.4472	1.4771	1.5051	1.5315	1.5563	1.6021
			In aqueous medium						
log kpz	14.34	15.24	16.18	17.12	18.45	19.01	20.78	21 72	22.67
E in K cals	23.4	24.5	25.8	26.8	28.6	29.1	31.4	32.4	33.6
			In 10% dioxan solution						
log kpz	9.10	9.62	10.15	11.46	11.98	13 36	15.09	16.44	17.81
E in K cals	17.1	16.7	17.3	18.0	18.6	21 8	23.6	25.3	27.1

TABLE 7—GELATION OF ALUMINIUM PHOSPHATE SOL B_3, ELECTROLYTE : POTASSIUM SULPHATE

			Temperature range 30°–45°						
log C × 10	0.4771	0.5441	0.6021	0 6532	0.6990	0.7404	0.7782	0.8457	0.9031
			In aqueous medium						
log kpz	15.66	16.61	17.96	19.77	21.13	23.71	25.08	26.04	27.01
E in K cals	25.90	27.1	28.8	31.1	32.8	36.3	38.0	39.1	40.0
			In 10% dioxan solution						
log kpz	11.98	12.91	15.09	15.64	17.38	19.96	22.58	–	–
E in K cals	19.6	20.7	23.6	24.2	26.5	29.9	33.4	–	–

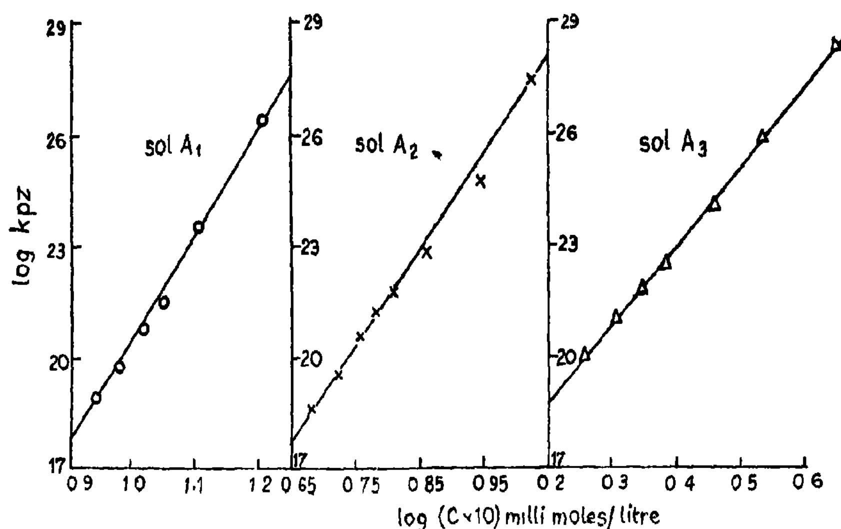


Fig. 2. Variation of log kpz with log C Sol ferric phosphate and electrolyte potassium sulphate.

the following relation for t_s or time for slow coagulation :

$\log t = N(\epsilon + V_{max})/2.3\ RT + B$ ..(11), where ϵ is the activation energy related to the attraction of the molecules of water i.e. viscosity of the medium, V_{max} is the maximum in the potential energy curve for the two interacting colloidal units and B a constant. Obviously, relations (8) and (11) are similar for a particular concentration of the electrolyte and $N(\epsilon + V_{max})$ of equation (11) is identical to E of equation (8). It will be seen from our data presented here and also those obtained earlier by Ghosh and co-workers[4,8] for several other sols that E continuously increases with increasing concentration of the electrolyte, but V_{max} should decrease because of the decreasing electric charge on colloid particles.

In Fig. 3, the effect of the rate of gelation or coagulation on the value of activation energy has been shown. It is seen that for slow coagulation the values of E slowly increase with the increasing rate and as the rate tends to become rapid the activation energy also sharply increas[es]. It appears that E is more related to the fr[ee] surface energy than the electric charge on t[he] dispersed particle or V_{max} of the potential ener[gy] curve With larger concentrations of the electroly[te] the charge on the colloid particles is more or le[ss] neutralised and primary and finer particles agglom[e]rate rapidly yielding coarser ones of smaller surfa[ce] energy for which higher activation energy is requir[ed] for their further agglomeration.

From Fig. 3, the value of E_0 or the activati[on] energy when the rate of coagulation or gelati[on] is slowest for sol A_1 can be evaluated. Similarl[y] the values of E_0 for other sols A_2, A_3, B_1, B_2 a[nd] B_3 have been obtained. The values of E_0 for t[he] sols investigated here are noted in Table 8, and it [is] found that for sols yielding gels the value of E_0 [is] more than 20 K cals, whilst for the sols B_1 and B[...] which produce bulky coagula, it is comparative[ly] less. No doubt the gel yielding colloid particles a[re] highly solvated and thus their surface energy [is] considerably moderated. For a truely lyophobic s[ol]

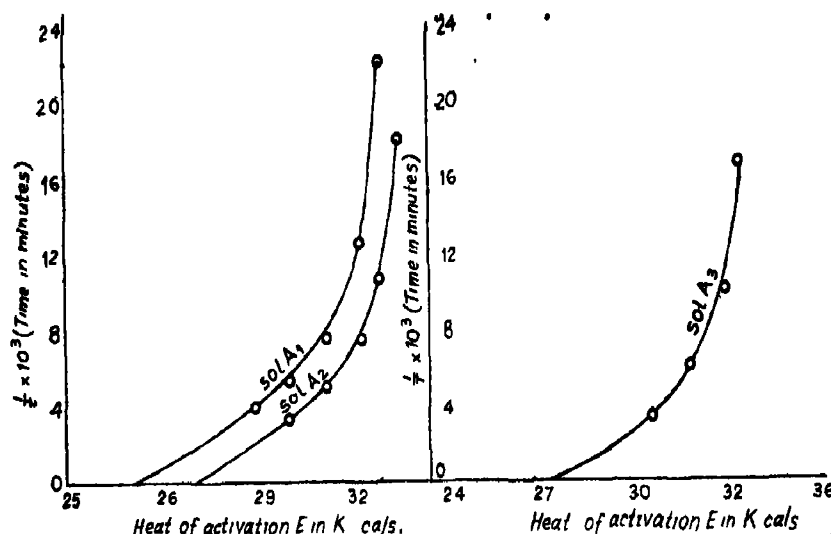


Fig. 3. Sol. ferric phosphate ; electrolyte potassium sulphate : plot of E vs $^1/T$ (Temperature 35°).

as that of silver the value of E_0 has been found to be 8 K cals[4a].

TABLE 8

Sol	A_1	A_2	A_3	B_1	B_2	B_3
E_0 (K cals)	25.0	27.0	27.5	16	20	21
Nature of the coagulum	gel	gel	gel	bulky coagulum	very bulky coagulum	hazy gel

Addition of dioxan to the sols investigated here considerably affects the precipitation or gelation values for an electrolyte, i.e. the sols become unstable. Dioxan lowers the dielectric constant of water. Obviously this lowering of the dielectric constant compresses the double layer of the charged particles and these may now approach nearer and come within their attractive range. Such condition is also created when an electrolyte is added to a sol. Our experimental data show that as more and more of an electrolyte is added to a sol the activation energy tends to increase and as the coagulation or gelation becomes rapid it sharply increases. It is interesting to find that dioxan increases the rate of gelation or coagulation effected by a definite concentration of the electrolyte, but the activation energy is remarkably decreased. This suggests that the lowering of dielectric constant increases the free surface energy of the colloid particles composed of the phosphates of iron or aluminium. Ghosh and Sengupta[14] studied the effect of dioxan on negatively charged sulphur sols (prepared by two different methods) and reported that these sols become very sensitive to electrolytes in the presence of dioxan, but the activation energy increased considerably.

A perusal of Table 1 will show that the rate of gelation of ferric phosphate by an electrolyte becomes about four times or more for 10° rise in temperature. This itself suggests that an "activated aggregate" is first formed by the collision of colloidal particles of sufficient energy (activation energy) and that such an "activated aggregate" yields a stable aggregated particle depending upon the probability factor p The stability of a lyophobic sol towards an electrolyte therefore depends upon the values of E and p.

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The Relation Between Intensity and Velocity of Photo-Chemical Reactions

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The relationship between intensity and velocity of a photochemical reaction can vary from direct to square-root. For reactions in which the primary process directly gives rise to final products, the extent of activation determines the relationship. If there is a chain mechanism, the order of the reaction with respect to chain carriers in the chain termination stage determines this relationship [and not the total molecularity of this stage]. If the molecularity with respect to chain carriers is unity, the direct relationship between intensity and velocity is likely to exist. If the order with respect to chain carriers is bimolecular square-root relationship is likely to be observed. By varying intensity and concentrations and the nature of reactants [over a wide range], the same reaction may be made to show a relationship extending from direct to square-root.

BHATTACHARYA and Dhar[1] classified photo-chemical reactions into the following three groups :

(i) The reactions in which the velocity tends to be directly proportional to the square-root of the intensity.

(ii) The reactions in which the velocity tends to be directly proportional to the intensity.

(iii) The reactions in which the velocity tends to be proportional to the square of the intensity.

Bhagwat[2] and Bhagwat and Dhar[3] deduced a theoretical expression for the relation between intensity and velocity of photo-chemical reactions from the view point of activation. If the intensity is varied in 'n' equal stages, and 'A' is the total number of molecules, 'x' the number of active molecules originally present before exposure, and 'y' is the fraction of inactive molecules activated each time by exposure, the photo-chemical acceleration in the first stage is proportional to $(A-n)y$ and in the 'n'th stage it is proportional to $(A-x)[1-(1-y)^n]$.

It is evident from above, that 'y' becomes very small, if photo-chemical acceleration over the dark reaction is very small. Moreover 'y' is a fraction less than unity. Hence, higher powers of 'y' in the expansion of $(1-y)^n$ as square etc may be neglected. The photo-chemical acceleration in the 'n'th stage is therefore proportional to

$$(A-x)[1-(1-ny)] \text{ or } n(A-x)y$$

Hence, when the photo-chemical acceleration is in the 'n'th stage or when the intensity is increased n fold, the acceleration is n times the acceleration in the first stage. Thus, when the photo-chemical acceleration is small, the velocity is directly proportional to the intensity. However, higher powers of y cannot be neglected when y is large and hence the velocity-intensity relation is less than unity or approaches square-root relationship.

Thus, when the absorption of the radiation is higher and the reaction is not markedly photo-chemical in nature and the velocity of the reaction in the dark is appreciable, direct proportionality is likely to be observed. On the other hand when the reaction is highly photo-chemical in nature and the velocity of the dark reaction is practically negligible, square-root relationship is to be expected.

The above theoretical expression brings out the important fact that the relation between intensity and velocity can never exceed unity. In other words, the square relationship suggested by Bhattacharya and Dhar[1] is not possible.

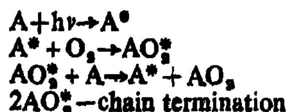
Practically in all cases the observed relationship is either unity or less than unity. The only peculiar case is that observed by Baly and Barker[4] with the photo-chemical combination of hydrogen and chlorine, where a relationship greater than unity was observed. Bhattacharya and Dhar[1] also observed such a relationship in a few cases where special attempts were made to reduce the photo-chemical acceleration by adding such inhibitors as potassium bromide or potassium iodide. These deviations were explained by us on the ground that in initial stages, part of light energy absorbed is used in destroying the inhibitors and the whole absorbed energy is not responsible for the photo-chemical reaction. When intensity is increased the proportionate loss of energy in destroying the inhibitors becomes smaller and smaller and hence apparently it appears that the rate of the photo-chemical reaction is proportional to a power of intensity greater than unity. Baly and Barker[4] admitted that their reacting gases were impure.

Thus the relationship between intensity and velocity could be one or less than one only.

The above discussion is applicable to cases where the primary process directly results into the final products of the reaction.

Our views of the photo-chemical reactions with chain mechanism are to be modified. It seems that in these cases the relationship between intensity and velocity is guided by the chain terminating reaction. This will be clear from the following examples.

(i) In case of photo-chemical oxidation of acetaldehyde studied by Bowen and Tietze[5] the mechanism suggested is



$A + h\nu \rightarrow A^*$
$A^* + O_2 \rightarrow AO_2^*$
$AO_2^* + A \rightarrow A^* + AO_2$
$2AO_2^*$ — chain termination

A represents acetaldehyde and AO_2 the oxidation product. The chain terminating reaction is,



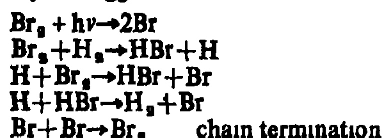
$2AO_2^* \rightarrow$ products

The rate of reaction on the basis of this mechanism is given by

$$\frac{d[AO_2]}{dt} = K\sqrt{I}\,[A] \qquad \text{... (i)}$$

or the velocity of the photo-chemical reaction is proportional to the square root of the intensity.

(ii) Similarly for the photo-chemical reaction between hydrogen and bromine, Bodenstein and Lütkeymeyer[6] suggested the mechanism.



$Br_2 + h\nu \rightarrow 2Br$
$Br_2 + H_2 \rightarrow HBr + H$
$H + Br_2 \rightarrow HBr + Br$
$H + HBr \rightarrow H_2 + Br$
$Br + Br \rightarrow Br_2$ chain termination

The rate of reaction by this mechanism is given by

$$\frac{d[HBr]}{dt} = \frac{K\sqrt{I}\,[H_2]\,[Br_2]}{K_1[Br_2] + [HBr]} \qquad \text{... (ii)}$$

This holds for constant pressure.

In this case the velocity of the photo-chemical reaction is proportional to the square root of the intensity. If the chains terminate at walls as



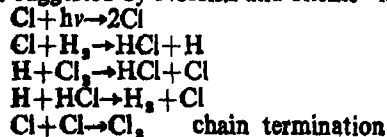
Br (wall) - - - ½ Br_2 (wall)

the rate of the reaction is given by

$$\frac{d[HBr]}{dt} = \frac{4\,I\,[H_2]}{K_5\left\{1 + \frac{K_3\,[HBr]}{K_5[Br_2]}\right\}} \qquad \text{... (iii)}$$

and the velocity of the reaction is now directly proportional to the intensity.

(iii) In case of the photo-chemical reaction between hydrogen and chlorine free from oxygen, the mechanism as suggested by Norrish and Richie[9] is



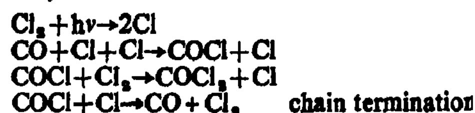
$Cl + h\nu \rightarrow 2Cl$
$Cl + H_2 \rightarrow HCl + H$
$H + Cl_2 \rightarrow HCl + Cl$
$H + HCl \rightarrow H_2 + Cl$
$Cl + Cl \rightarrow Cl_2$ chain termination

and the rate of the reaction is given by

$$\frac{d[HCl]}{dt} = \frac{2K_2\,K_3\sqrt{K_1/K_5}\,[H_2]\,[Cl_2]\sqrt{I}}{K_3\,[Cl_2] + K_4[HCl]} \qquad \text{... (iv)}$$

Thus the rate of the reaction is proportional to the square root of intensity.

(iv) The mechanism suggested by Lender an[d] Rollefson[8] for the photo-chemical formation o[f] phosgene is,



$Cl_2 + h\nu \rightarrow 2Cl$
$CO + Cl + Cl \rightarrow COCl + Cl$
$COCl + Cl_2 \rightarrow COCl_2 + Cl$
$COCl + Cl \rightarrow CO + Cl_2$ chain terminatio[n]

The rate of the reaction is given by

$$\frac{d[COCl_2]}{dt} = k\sqrt{I}\,[CO][Cl_2] \qquad \text{... (}$$

or the velocity of the reaction is proportional to t[he] square root of the intensity.

It will be clear from these observations that i[n] cases (i), (ii), (iv) and (v) where the chains termina[te] bimolecularly, the rate of the reaction is propo[r]tional to the square root of the intensity, while it [is] directly proportional to the intensity where th[e] chains terminate unimoleculary as in the case (iii[)]. Thus if concentration of the radicals is high, bimo[]lecular termination in the gas phase is favoure[d] while for low concentration, the termination is mo[re] likely to occur unimolecularly at the wall and th[e] direct relationship between velocity and intensity [is] likely to be observed. By changing intensity an[d] concentration of the reactants over a wide range [it] is possible to get relationship from direct to squa[re] root for the same reaction.

The above statement needs modification. Cons[i]der the following chain reactions and their cha[in] termination process.

(i) The chain termination in case of oxidation o[f] aldehydes in presence of alcohol is bimolecular[9] a[s]



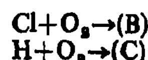
$AO_2^* + X$(alcohol) chain termination .(A)

but the rate of the reaction is given by

$$\frac{d[AO_2]}{dt} = \frac{K^1[A]\,I}{[X]}$$

or there is direct proportionality between intensi[ty] and velocity of the reaction.

(ii) Similarly in case of hydrogen chlorine reactio[n] in presence of oxygen the chains terminate bimol[e]cularly as



$Cl + O_2 \rightarrow (B)$
$H + O_2 \rightarrow (C)$

But the rate of the reaction is given by[10]

$$\frac{d[HCl]}{dt} = \frac{K\,I\,[Cl_2]}{[O_2]} -$$

and $$\frac{d[HCl]}{dt} = \frac{4\,K_2K_3\,I\,[H_2]\,[Cl_2]}{[O_2]\,(K_3\,K_4\,[H_2] + K_2K_5\,[Cl}$$

or the velocity is directly proportional to intensity.

(iii) The behaviour of $H_2 + Br_2$ reaction at varyin[g] pressure is similar. Here the chains terminate as



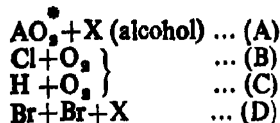
$Br + Br + X \rightarrow Br_2 + X$ ... (D)

where X is any molecular species present whic[h] removes energy. The reaction is termolecular an[d] the rate of the reaction is given by[11]

$$\frac{d[HBr]}{dt} = \frac{k\sqrt{I}\,[X]\,[H_2]\,[Br_2]}{K_1\,[Br_2] + [HBr]}$$

or square root relationship exists between intensity and velocity and not $I^{1/3}$ relationship, though the reaction is termolecular.

The above discussion will make it clear that it is not the total molecularity of chain reaction that determines the relationship between intensity and velocity if we consider the chain terminating processes discussed above,



$AO_2^* + X$ (alcohol) ... (A)
$Cl + O_2$ ... (B)
$H + O_2$ ... (C)
$Br + Br + X$ ... (D)

We observe that [X] or [O_2] are not chain carriers In case v, both COCl and Cl are chain carriers, though they are different. Thus it is the molecularity with respect to chain carriers that is significant in determining the relationship between velocity and intensity of a particular photochemical process and not the total molecularity of the chain terminating reaction Thus the reactions (A), (B) and (C), though bimolecular as a whole, are unimolecular with respect to chain carrier and hence direct relationship between intensity and velocity is observed. The reaction (D) as a whole is termolecular but is bimolecular with respect to chain carrier. Hence the square root relationship between intensity and velocity exists.

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Concentration Depolarization, Energy Transfer and Kinetics of Concentration Quenching of Fluorescence of Anthracene Sulfonates

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ANTHRACENE sulfonates are known to undergo various photochemical changes like photoperoxidation[1] and photodimerization[2]. They have also been used as singlet oxygen sensitizer[3] and as suitable probes for polarity of the medium[4]. The luminescence properties of dissolved substances depend essentially on concentration. Therefore to substantiate such studies it is necessary to evaluate various parameters relating to selfquenching, if any.

Apart from trivial radiative inner filter effect, increase in the concentration of the molecules taking part in emission processes may lead to depopulation of excited state by nonradiative processes also, causing reduction in the fluorescence quantum efficiency without any drastic alteration in the fluorescence spectrum. The absorption spectrum remains unchanged but the fluorescence lifetime is reduced. Förster[5] has identified four types of quenching mechanisms which can be characterised by the effect of concentration on fluorescence decay times, and viscosity and temperature dependence of fluorescence efficiency. In any one system more than one mechanism may be operative, the boundaries between them being not very strictly defined.

Basically all types of quenching involve complex formation of some kind in their ground or excited states. The ground state complex formation leads to static quenching and is not truly excited state phenomenon. The complexes formed in the excited state are termed exciplexes. One of the mechanisms suggested for concentration quenching is through the formation of excimers, the dimers formed in the excited state by collision between an excited and a ground state molecules[6].

The phenomenon was first observed in pyrene molecules[7]. Such excimers have large radiative lifetimes and enhanced nonradiative decay probabilities. The system obeys diffusion-controlled kinetics. In the other extreme is the long range resonance energy transfer mechanism of Förster. In the long range energy transfer mechanism, the migration of energy from molecule to molecule is brought about by dipole-dipole interaction and may not lead to quenching by itself. It is necessary to have an energy sink or trap. In many systems such traps are provided by trace amounts of aggregates present in solution. This is the important mechanism in plant photosynthesis where energy absorbed by antennae chlorophyll molecules is transferred to the reaction centre which is suggested to be a chlorophyll dimer[8]. The nonradiative resonance transfer may take place at distances greater than around 15Å. At closer distances (< 15 Å), electron exchange mechanism may become operative[9].

The excimers may be fluorescent or nonfluorescent. The nonfluorescent excimers cause immediate quenching whereas fluorescent excimers of aromatic hydrocarbons emit at a longer wavelength shifted by about 6000 cm^{-1} to red from the monomer band. The excimer formation is reversible and diffusion controlled phenomenon, affected by temperature and viscosity, and requires a minimum distance of approach of the order of 3.4 Å of the two partners. Nonfluorescent excimers also require close approach and hence concentration quenching is prevented in molecules with bulky substituents such as is the case for 9,10-diphenyl anthracene[10,11]. When the interaction is strong, photodimerisation may result[10]. Concentration quenching may involve either decrease in the rate constant of radiative process or increase in the rate constant of nonradiative processes or both, depending upon the system under study.

Geometrical requirement for excimer formation leading to quenching is not always clear. Anthracene excimers[11] are known to have two types of structures (i) sandwich structure and (ii) 55° structure. The former may lead to photodimer formation whereas the latter may just cause self quenching since the geometry is not suitable for bond formation. The 55° dimer is the more stable type (Fig. 1). In the absence of photodimer formation, the excimer may relax by dissociating into two ground state molecules or by emission of

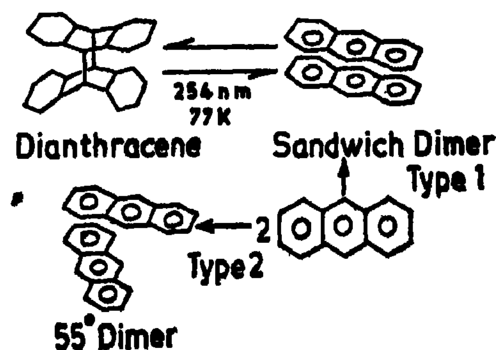


Fig. 1. Geometry of anthracene photodimer and excimer.

red shifted excimer fluorescence leading to quenching of monomer fluorescence.

The dipole-dipole energy transfer is demonstrated in concentration depolarization of fluorescence whereas collisional quenching follows simple Stern-Volmer kinetics[12] expressed as

$$\phi_f^0/\phi_f = 1 + k_q\tau\,[Q] = 1 + K_{sv}\,[Q] \qquad \ldots (1)$$

where ϕ_f^0 and ϕ_f are the quantum yields of fluorescence, in absence and in presence of quencher of concentration [Q] respectively, K_{sv} is the Stern-Volmer quenching constant and k_q is the rate constant measured for bimolecular quenching process.

For a diffusion controlled process[13] the rate constant of a bimolecular reaction can be expressed by the Einstein-Smoluchowski[13] equation based on Fick's law of diffusion

$$k_{diff} = p\,\frac{4\pi NDR}{1000}\left(1+\frac{pR}{\sqrt{\pi D\tau}}\right)\ M^{-1}s^{-1} \quad \ldots (2)$$

The factor within the bracket accounts for the transient quenching effect and is normally of the order of unity, such that the equation reduces to a simple form

$$k_{diff} = p\,\frac{4\pi NDR}{1000} \qquad (3)$$

where D is the sum of the diffusion coefficients of the two interacting partners, $R=(r_a+r_b)$ is the sum of the two interaction radii and p is the probability of quenching per encounter. For collisional quenching, interaction radii is identified with the molecular radii, r. When the effects of electrostatic interactions due to charged species are introduced[14], the equation becomes,

$$k_{diff} = p\,\frac{4\pi NDR}{1000}\cdot\frac{\delta}{e^{\delta}-1} \qquad . \ (4)$$

with $\delta = Z_A Z_B\, e^2/\epsilon\,(r_a+r_b)\,kT$, where ϵ is the dielectric constant of the solvent, Z_A and Z_B are the numbers of charges with proper sign on the molecules A and B respectively. In the case of concentration quenching the fluorescer and the quencher are molecules of the same kind and $R=2r$ and $D=2D_a$; quenching involves specific interaction to dissipate the energy along nonradiative pathways.

The quantum mechanical formulation of energy transfer by Förster[15] requires that the absorption spectrum of the acceptor must overlap the emission spectrum of the donor. The efficiency of intermolecular dipole-dipole transitions may be expressed in terms of a critical transfer distance, R_0, at which probability of transfer is equal to the probability of decay of the excited molecule by all other modes as expressed by the decay constant, $\tau=(\Sigma k_i)^{-1}$. From the Förster equation, R_0 is expressed as follows :

$$R_0^6 = \frac{9000(\ln 10)\,\kappa^2\phi_f}{128\pi^5 n^4 N}\ \frac{\int_0^\infty \frac{F(\tilde\nu)\,\epsilon(\tilde\nu)}{\tilde\nu^4}\,d\tilde\nu}{\int_0^\infty F(\tilde\nu)\,d\tilde\nu}$$

in which N is the Avogardo's number ; n is the refractive index of the medium κ^2 is an average orientation factor resulting from the rapid rotatory Brownian motion of the donor and acceptor ($\approx 2/3$), $\int F(\tilde\nu)\,d\tilde\nu$ is the fluorescence emission spectrum of the donor expressed in wavenumber and normalized to unity, $\epsilon(\tilde\nu)$ is the molar extinction coefficient of the acceptor.

The critical transfer distance for energy transfer by dipole-dipole mechanism can be experimentally obtained from the measurements of polarization degree as a function of concentration C mol l^{-1}. The expression given by Weber[16] for concentration depolarization effect is

$$\left(\frac{1}{p}-\frac{1}{3}\right) = \left(\frac{1}{p_0}-\frac{1}{3}\right)\left[\,1+\frac{4\pi\,NR_0^6\times 10^{-3}}{15\,(2r)^3}\,C\,\right] \ldots (6)$$

$$\text{so that, } R_0 = (2r)^{\frac{1}{2}}\left[\frac{15\,S\,10^3}{4\pi N\left(\frac{1}{p_0}-\frac{1}{3}\right)}\right]^{\frac{1}{6}} \qquad \ldots (7)$$

where S is the slope of $\left(\frac{1}{p}-\frac{1}{3}\right)$ vs C plot and 2r is the molecular diameter

Materials and method :

Anthracene 1- and 2-monosulfonates and 1,5- and 1,8-disulfonates, abbreviated as 1-AS, 2-AS, 1,5-AS and 1,8-AS, were prepared from corresponding quinones by the method described earlier[1]. Glycerol (B.D.H.) was distilled twice under reduced pressure and emission impurities were checked.

Absorption spectra were measured manually by Perkin-Elmer spectrophotometer, Model Hitachi 200. The fluorescence spectra were recorded with a Perkin Elmer MPF 44 B spectrofluorimeter.

The fluorescence intensity at different concentrations of anthracene sulfonates were measured at an angle 90° to the direction of incidence in a Brice Phoenix Universal Light Scattering instrument model 1000 series, with suitable primary and secondary filters. A HP Hg-discharge lamp (85 watts), type AH-3, was used as the excitation source. 365 nm line of mercury was selected for excitation. The solutions were taken in 1 cm all side clear silica cell. The cell was covered with black paper on two adjacent sides leaving only a small opening (0 3 cm width, 0 4 cm height) in the direction of excitation as well as in the direction of observation. The edge of the cell at the joint portion was also covered with black paper to avoid scattered and reflected light. In effect, the total fluorescence was measured from the solution of volume 0 3×0 3×0 4 ml.

Such arrangement is expected to minimise error due to re-absorption and re-emission and to also diminish the area of incomplete illumination within the area of observation at high concentrations of fluorescer. As the overlap integrals of the absorption and emission spectra of these sulfonates are small, specific correction for re-absorption and re-emission

suggested by Rohatgi and Singhal[17] was not applied. An interference filter (413 nm) was placed before the photomultiplier to cut off the overlap region of the emission spectrum to further minimise the re-absorption and re-emission errors in the measurement of fluorescence.

Fluorescence polarization intensities were measured in the same instrument at right angles to the direction of propagation of the incident light. The solutions in glycerol (90%) were excited by both vertically and horizontally plane polarized light of wavelength 365 nm, obtained by using polarizer supplied with the instrument. Both, horizontal and vertical components of the fluorescence light were measured by using the analyzer.

The degree of polarization (P) was determined by using the refined expression proposed by Azumi and McGlynn[18].

$$P = \frac{I_{EE} - I_{EB}\,(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})}$$

where E represents the polarization direction with electric vector perpendicular to the plane formed by the excitation beam and the observation beam: B represents polarization direction with electric vector in the plane formed by the excitation beam and the observation beam.

Results and Discussion

The Stern-Volmer plots ϕ°_f/ϕ_f vs C, for anthracene 1- and 2-mono sulfonates and 1,5-and 1,8-disulfonates in water are given in Fig. 2. For the measurement of ϕ_f, $10^{-5}M$ solution of ea anthracene sulfonate in the corresponding solve was taken as standard. Corrections for re-absor tion, re-emission, refraction and the geometry of t experimental set up was taken into consideration.

In aqueous solution the concentration quenchi of all these anthracene sulfonates obeys the Ster Volmer equation. But in glycerol solution measurable amount of quenching was observed a the slope of the S-V plot was negligibl . S quenching constant, K_{sv}, for concentrati quenching was measured directly from the slope a the experimental rate constants for concentrati quenching (k_q^{exp}) were obtained from the equation

$$k_q^{exp} = \frac{K_{sv}}{\tau} \qquad \dots ($$

where τ is the lifetime obtained by single-phot counting technique reported earlier[10]. The ra constant for concentration quenching, k_q^{exp}, aqueous solution so obtained experimentally for the anthracene sulfonates are given in Table column 5. They are of the same order as that f anthracene 9.3×10^9, 9.7×10^9 and 11.7×10^9 mol s^{-1} in benzene, chloroform and kerosene respective obtained by Bowen *et al*[19]. The low value of K but high value of rate constant (15×10^9) for 1,8-A is expected because of its very low lifetin (τ=1 45 ns) and quantum yield (ϕ°_f=0.16) compared to anthracene and other sulfonate Similar observation was made by Bowen[19] for 1,

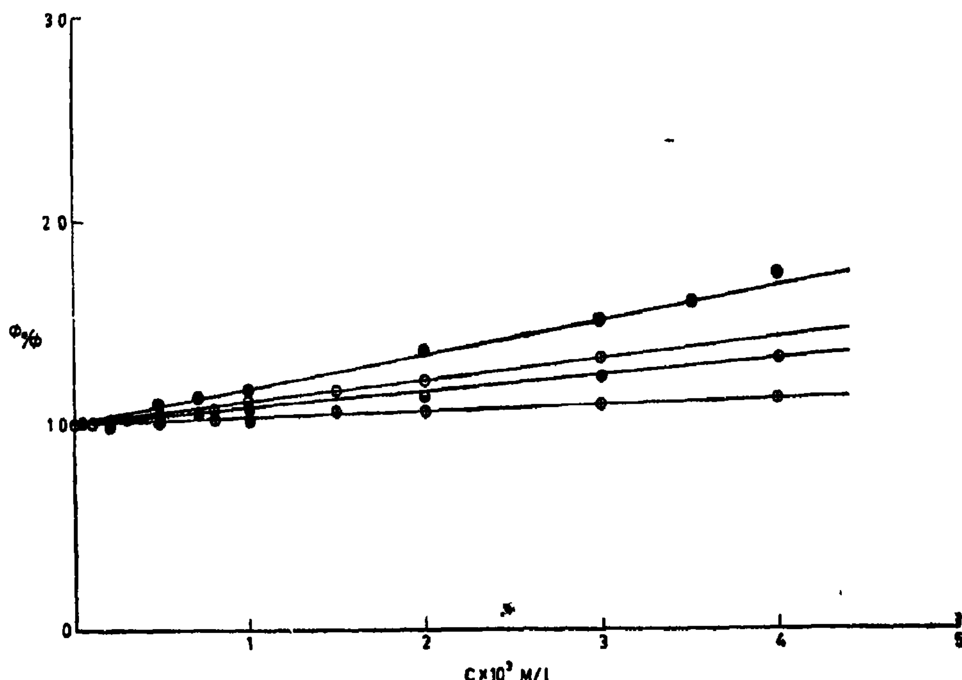


Fig. 2. Stern-Volmer plots : ϕ°_f/ϕ_f vs C for different anthracene sulphonates in water at 30°.

●→1-AS
⊙→2-AS
◐→1,5-AS
⊗→1,8-AS

dichloro anthracene whose K_{sv} was found to be small ($K_{sv}=11$) mainly because of small value of fluorescence efficiency. On the other hand, K_{sv} for coronene ($K_{sv}=650$) is large because of its long lifetime in the excited state. The K_{sv} values of a number of anthracene derivatives in solvents like benzene, chloroform and kerosene are observed[18] to lie between 10 to 100 which supports the value of our experimentally determined S-V quenching constant of anthracene sulfonates. The systems under study were not deoxygenated.

For anthracene sulphonates, charge and solvent dielectric properties are also important. The quenching of 1,5- and 1,8-disulfonates is less efficient than that for 1- and 2-monosulfonates in water evidently due to two units of negative charge and consequently greater electrostatic repulsion. For 1,8-AS such repulsion is expected to be greater than 1,5-AS due to two negative charged groups at the same side of the ring. Consequently, its slope for concentration quenching is very small. Assuming concentration quenching of fluorescence of anthracene sulphonates to occur by diffusion controlled process only, a theoretical value of the rate constant can be calculated for each system using eqn (4). The k_q^{theo} values are presented in column 6 of Table 1 for two different solvents water and glycerol. Experimental K_{sv} and k_q^{exp} obtained in water are reported in columns 4 and 5 respectively.

values. The anomaly is likely to be due to pR values which may be much larger than the assumed collision radii with p=1. This indicates that long range dipole-dipole mechanism of Förster type is also involved in concentration quenching. Very low calculated values of k_q^{theo} in glycerol are understandable since the probability of diffusion-controlled encounter formation will be very small in such viscous solvents.

Theoretical formalism for diffusion-controlled reaction is under rescrutiny by Ware *et al*[20]. The models have been developed[21] which allow calculation of rate constants for systems which follow partly diffusion controlled kinetics. For the systems with excited state lifetimes shorter than 100 ns and in conventional solvents, nonstationary processes also become important which require apparent rate constants to become time dependent. The classical expression for apparent rate constant k(t) is then expressed as

$$k(t)=p4\pi\, D\sigma N'\left[1+\frac{\sigma}{(\pi Dt)^{1/2}}\right] \quad \dots (9)$$

where σ=encounter distance and $D=D_a+D_b$. The term within the bracket, which corrects for the transient quenching, will become important for times shorter than σ^2/D or near this value At times much longer than this, k(t) is approximately equal to $4\pi N\sigma D$, and steady state diffusion takes place.

TABLE 1

Compound	$\phi_f^{0(a)}$	τ ns Single photon method	$K_{sv}^{(b)}$ l mol^{-1}	$k_q^{exp} \times 10^{-9(c)}$ l mol^{-1}s^{-1}	$k_q^{theo} \times 10^{-9(d)}$ l mol^{-1}s^{-1}
(1)	(2)	(3)	(4)	(5)	(6)
1-AS	0.25	7 30	80(W) –	10 9(W) –	2 6 (W) 0 0044 (G)
2-AS	0.40	4 50	50(W) –	11 1(W) –	2 6 (W) 0 0044 (G)
1,5-AS	0.26	3.22	27(W) –	8 3(W) –	1 24 (W) 0 0002 (G)
1,8-AS	0.16	1.46	22(W) –	15 0(W) –	1 24 (W) 0 0002 (G)

(a) A. K. Gupta and K. K. Rohatgi-Mukherjee, Ref. 3.
G – glycerol, W – water
(b) Calculated from equation (1), (c) Calculated from equation(8),
(d) Calculated from equation (4), using r (1-AS and 2-AS) – 4.27 Å and r (1,5-AS and 1,8-AS) – 4.63 Å : D (1-AS and 2-AS) – 6.4×10^{-6} cm^2/sec in water and 8.1×10^{-9} cm^2/sec in glycerol and D (1,5-AS and 1,8-AS) – $5\,9\times10^{-6}$ cm^2/sec in water and $7\,50\times10^{-9}$ cm^2/sec in glycerol.

The experimental values of rate constant for anthracene sulfonates are higher than the theoretical values measured for the diffusion controlled limiting expression including charge effect as shown in Table 1. These differences may be expected due to the value of 'r' which may still need some correction as solvation effect has not been taken into consideration. The value of diffusion co-efficient calculated from r value obtained by density data also introduce some error. There may be some error due to re-absorption re-emission phenomenon.

These corrections, however, cannot explain the large differences in theoretical and experimental

The instantaneous rate constant is then time independent For 1-AS

$$\tau_0=\frac{\sigma^2}{2D_a}=\frac{(8\,54)^2\times10^{-16}\,\mathrm{cm}^2}{2\times0\,64\times10^{-5}\,\mathrm{cm}^2\mathrm{s}^{-1}}=5\,7\times10^{-10}\mathrm{s} \quad \dots (10)$$

The lifetime of 1-AS, $\tau=7\,4\times10^{-9}$, is greater than this critical time τ_0 by an order of magnitude. The transient term may not contribute much to the overall rate constant. If at all, the transient term may have some contribution to make for 1,5-AS and 1,8-AS whose lifetimes are 3.22 and 1.46 ns, respectively. The values of $\left(1+\frac{p\sigma}{\sqrt{\pi D\tau}}\right)$, assuming p=1,

$\sigma=2r$ and $D=2D_s$, are 1.16, 1.20, 1.30 and 1.45 for 1-AS, 2-AS, 1,5-AS and 1,8-AS respectively.

On expanding the equation (9), we obtain

$$k=4\pi N'D(p\sigma)+\frac{4\pi N'D}{\sqrt{\pi D\tau}}(p\sigma)^2$$

which when multiplied throughout by the lifetime τ becomes

$$k\tau=4\pi N'D\ (p\sigma)\tau+\frac{4\pi N'D}{\sqrt{\pi D\tau}}(p\sigma)^2\tau$$

$$K_{sv}=4\pi N'D\tau(p\sigma)+4N'\sqrt{\pi D\tau}\ (p\sigma)^2$$

On rearranging and introducing the charge factor $B\left(=\frac{\delta}{e^{\delta}-1}\right)$ a quadratic equation is obtained:

$$4N'\sqrt{\pi D\tau}\ B\ (p\sigma)^2+4\pi N'D\tau B\ (p\sigma)-K_{sv}=0$$

which is of the form

$ax^2+bx+c=0$ where $x=p\sigma$ and is given by

$$x=\frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

and $a=4N'B\sqrt{\pi D\tau}$, $b=4N'B\pi D\tau$, $c=-K_{sv}$

The values of $p\sigma$ so calculated are reported in Table 4, column 2. The values 7.43 Å, 13.5 Å, 32.2 Å and 40.7 Å for 1-AS, 2-AS, 1,5-AS and 1,8-AS are far different from kinetic collision radii.

On the other hand, the critical transfer distance R_0 between molecules fixed in position in viscous medium can be calculated from spectroscopic data using Förster equation[18]. Assuming $\langle\kappa^2\rangle = 2/3$ which implies that the rotational lifetime for the solute molecules is much smaller than the actual radiative lifetime τ, the values of R_0 in Å and critical concentration C_0 in mol per litre are given in Table 2. C_0 values were calculated from the relationship

$$C_0=\frac{1}{V_0}=\frac{3000}{4\pi R_0^3 N_0}$$

TABLE 2

Compound	$J(v)\times10^{16}$ M^{-1} cm^6	R_0 Å	$C_0\times10^3$ M/l
1-AS	13 56	19	5 7
2-AS	14 63	20	4 9
1,5-AS	15 61	19	5.7
1,8-AS	7.35	17	8 0

assuming R_0 to be the radius of a sphere with the excited molecule in the centre and only one quencher molecule within the sphere. The overlap integral was calculated graphically with the help of planimeter (Fig. 3).

R_0 values were also calculated from the data of concentration depolarization of anthracene sulphonates in glycerol solution. The plot of $(1/p_0-1/3)$ vs C according to Weber's equation (7) is shown in Fig. 4. The slope S of the straight line and R_0 values derived therefrom are given in Table 3.

TABLE 3

	1-AS	2-AS	1,5-AS	1,8-AS
$(1/p_0-\frac{1}{3})$	32	24	15	7
$S\times10^{-4}$	20.06	19.01	5.83	3.05
R_0 (Å)	45	46	43	44

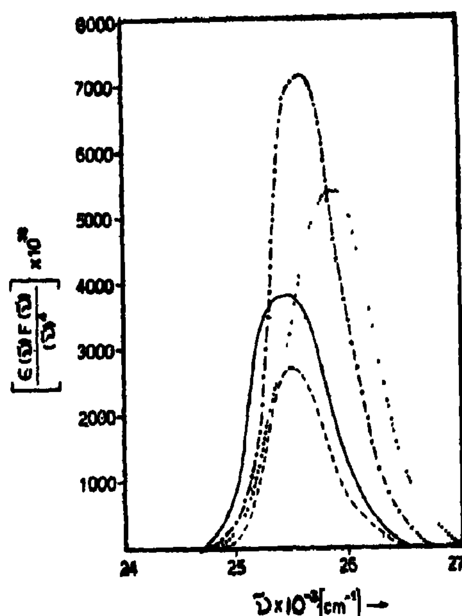


Fig. 3. Plots of $\epsilon(\bar{\nu})\ F(\bar{\nu})/\bar{\nu}^4$ vs $\bar{\nu}$ for different anthracene sulphonates. $\epsilon(\bar{\nu})$ is the molar extinction coefficient at wave number $\bar{\nu}$ cm^{-1} and $F(\bar{\nu})$ is the relative fluorescence quantum intensity at wave number $\bar{\nu}$ cm^{-1}.

——— 1-AS
. . . . .. 2-AS
—·—·— 1,5-AS
- - - - - 1,8-AS

According to dipole-dipole mechanism, the critical transfer distance R_0 in a solution is calculated on the assumption that the solute molecules are statistically distributed and fixed in a medium of infinite viscosity, so that energy transfer is a much faster process than mass transfer and rotational randomisation is complete. The spectra were measured in aqueous solution and the R_0 values were defined for 50% transfer efficiency. On the other hand, the R_0 values calculated from concentration depolarization data are much higher than those calculated from spectroscopic data. Such discrepancy has been observed previously also and has been discussed by Kawski[28]. Concentration depolarization arises due to hopping of excitational energy over molecules of different orientations before finally impinging on the photomultiplier detector. In the process, original orientation is lost leading to depolarisation. The effect increases with concentration. If rotational depolarization is superimposed on concentration depolarization, observed depolarization degree will be much higher. At the same time concentration quenching will reduce the radiative lifetime and decrease the depolarization degree. A large value

of R_0 will also be obtained when diffusion occurs along with energy transfer, i.e., the molecule is free to diffuse and transfer energy. The influence of diffusion on dipole-dipole transfer from anthracene to anthranilic acid in alcohols of various η have been studied by Elkana *et al*[23]. In the most viscous solvent (glycerol) they found an unexpected discrepancy between the values of R_0, 27Å obtained from energy transfer data and 22.4 Å obtained from spectroscopic data. They have shown that there is a variation of intermolecular distance between donor and acceptor, as a result of Brownian motion, during lifetime of the excited state. Theoretical approach to the problem of diffusional energy transfer is a field of active research[20,21,24].

The diffusion length $\sqrt{2D\tau}$, based on random walk model[24] for these molecules in aqueous solution and in glycerol are given in Table 4, column 5. The diffusion lengths in glycerol lie within 1.0 Å to 0.4 Å only i.e., the molecules are virtually fixed in position although Brownian movement of rotation is complete. In aqueous solutions $\sqrt{2D\tau} > R_0$, diffusional motion is considerable. All the data are collected in Table 4.

TABLE 4

	$p\sigma$ in Å	R_0 (Förster) in Å	R_0 depolarization in Å	$\sqrt{2D\tau}$ in Å	$\sigma + \sqrt{2D\tau}$ in Å
1-AS	7.43	19	45	30	37 4
2-AS	13 50	20	46	24	37.5
1,5-AS	32 20	19	43	19	51.2
1,8-AS	40.70	17	44	13	53 7

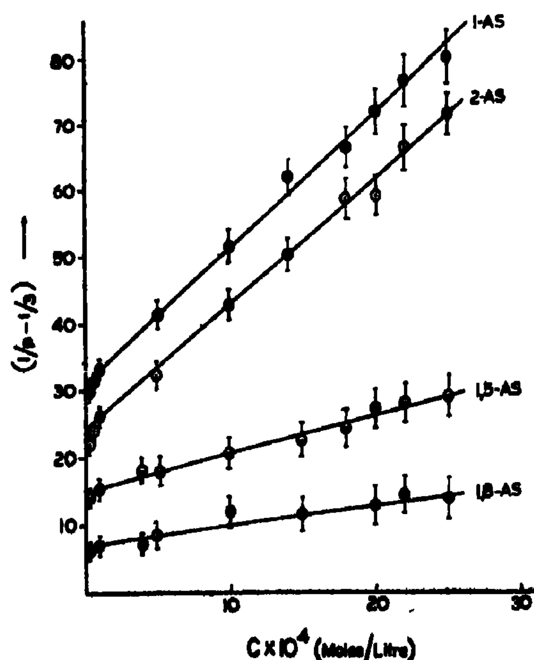


Fig. 4. Plots of (1/p−1/3) vs C for different anthracene sulphonates in 80% glycerol-water mixture at 30°.

The two situations, the reactions controlled by diffusion and the reactions controlled by resonance energy transfer, are examples of two extreme conditions : (i) the diffusional mixing is complete and the system obeys S-V kinetics and (ii) the molecules are fixed in position and energy transfer occurs by resonance interaction, Förster kinetics is valid. It is observed that concentration quenching is negligible in glycerol solution, the slope of S-V plot is nearly zero. This observation goes against the hypothesis of quenching by energy transfer. Normally one does not expect quenching when energy migrates from one molecule to another of the same kind. The concentration quenching in chlorophyll, which also shows much higher rate constant for quenching than that predicted by diffusion controlled mechanism, has been recently explained by Beddard and Porter[25,26] assuming quenching by energy transfer to those statistical pairs which are approximately 10 Å apart at the instant of excitation. The quenching occurs through excimer formation within such statistical pairs. Anthracene and their derivatives are known to form dimers and excimers[10]. Various substituted anthracene sulphonates also form photodimers although with low efficiency in deaerated solutions[9]. The low efficiency of photodimerization is likely to arise because of steric hindrance to sandwich configuration due to bulky SO_3^- groups but quenching may occur in nonsandwich configurations. If this mechanism is valid, there should be quenching in glycerol solution also. The life of such statistical pairs should be greater in viscous solvent as compared to a solvent of low viscosity. That energy transfer does occur between anthracene sulphonates is definitely established by concentration depolarization studies. These studies predict large critical transfer distances.

Concentration depolarization studies do not differentiate between transfer by single step or by a number of steps. The transfer distance from spectroscopic data using Förster equation is based on one step transfer. When $\tau_D^* > \tau_{ET}$ energy migration by excitation hopping creates a statistical distribution of excited centres $A^* + A \xrightarrow{k_{ET}} A + A^*$, with k_{ET} as the energy migration rate constant, Stern-Volmer kinetics can still be applied[27]. Since the experimental S-V plots are good-linear straight lines in all the systems, the interpretation of the data should be based on combined effect of diffusional quenching and excitation hopping. The non-radiative traps for quenching by energy transfer is likely to be ground state dimers which may be present in very trace amounts and hence not detectable spectroscopically. Yuen *et al*[28] has proposed a revised mechanism of concentration quenching in chlorophyll using the dimers as the energy traps. The existence of dimers and higher aggregates was established by very sensitive difference spectroscopy. The absence of quenching in glycerol solution is then due to inhibition of diffusional quenching due to high viscosity and

inhibition of quenching by energy transfer due to nonformation of aggregates. The flat anthracene moieties with hydrophilic substituent $-SO_3^-$ can form aggregates. Specially for 1,5-AS which has highest solubility amongst the sulfonates under study the observation is that for concentration variation between $10^{-5}-10^{-2}$ *M*, the fluorescence spectra remain unaltered in intensity and shape presumably due to aggregate formation[9]. Aggregate formation in napthalene sulphonate has been established by light scattering studies[29].

On examining the experimental value of $p\sigma$ derived from concentration quenching data, (Table 4, column 2), the values for monosulphonates are less than 15 Å. Assuming p=1, the interaction radii, $p\sigma$, is 7.5 Å for 1-AS and 13 Å for 2-AS, suggesting short range quenching by exchange mechanism. The energy dissipation within the encounter complex can be brought about through perturbation of energy levels of colliding partners which can promote forbidden transitions, hidden under the allowed energy state, by vibronic coupling. But for disulphonates, the large values of $p\sigma$ envisage long range energy transfer. Since the lifetimes of the molecules τ_{D*} are small, a hopping mechanism may be assumed before being trapped by a ground state dimer. Answer to the question as to why should monosulphonates and disulphonates should differ in the quenching step is not apparent immediately. Another interesting observation is that the experimental values of $p\sigma$ and diffusion-lengths $\sqrt{2D\tau}$ add up to constant values which is 37.5 Å for monosulphonates and 52·5 Å for disulphonates An explanation for this is also not available. In disulphonates, two units of negative charge present an electrostatic barrier to close approach recommending long range interactions, whereas monosulphonates can manage to come close together with specific orientation. The ground state dimers may be mere stacked species held together by π-π^* interaction or hydrogen bonded through $-SO_3$ groups and water molecules. Quenching by 55° dimers is also a possibility. Furthermore, in concentrated solutions the average orientation factor κ^2 may not be completely randomised[30] specially so in cases of the charged species.

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Photochemistry of Aqueous Anthraquinone-2-Sulfonate Solution

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The aqueous photochemistry of anthraquinone-2-sodium sulfonate (D) has been studied Under aerobic condition, mono-hydroxy derivative of D and hydrogen peroxide are the stable products of photolysis while in anaerobic medium mono-hydroxy derivative as well as semiquinone/semiquinolate ion are produced. In acid and neutral medium both α- and β-hydroxy derivatives of D are produced in the ratio 3 : 2, while in alkaline medium only the β-isomer is detected Quantum yields of hydroxy derivatives of D, semiquinone/semiquinolate ion and hydrogen peroxide are determined under both aerobic and anaerobic medium with (i) variation of initial concentration of D and (ii) variation of irradiation time.

The effect of some substrates namely sodium formate and sodium azide on the quantum yield of hydroxy derivative and the reduced product, semiquinone/semiquinolate ion has also been studied The results indicate that the formate here is not acting as a scavenger of OH radical, the precursor of hydroxy product, as suggested by some earlier workers but directly participates in the semiquinone formation On the basis of the results a mechanism has been suggested.

THE photochemistry of aqueous anthraquinone-2-Na-sulfonate (D) has been studied by various workers[1-7], yet this has continued to attract attention, particularly in relation to the phototendering effect of fabrics by anthraquinone dyestuffs[8]. Wells[9] first noted the formation of a coloured product (later detected to be hydroxy derivative of D), not removable by air oxidation, on irradiation of D in presence of water. Later, Mooney and Stonehill[1] reported the formation of semiquinone and mono-hydroxy derivative of D, on irradiation of aqueous alkaline D under anaerobic medium. Broadbent[3] extended the work to acid medium and pointed out that in dilute acid solution the products were a mixture of α- and β-hydroxy derivatives of D. Moreover, the formation of hydroxy-benzoic acid on irradiation of aqueous solution of D in presence of benzoic acid led them to suggest the intermediacy of OH· radical, produced by electron abstraction by the excited quinone from water, as

$$D+H_2O \xrightarrow{h\nu} D^{\cdot-}+H^{+}+OH$$
$$D+OH^{\cdot} \longrightarrow \text{hydroxylated product}$$

The formation of phenol[3], on irradiation of D containing benzene, also seemed to provide further evidence for participation of hydroxyl radical.

Clark and Stonehill[5], on the basis of the observations that (i) the rate of photohydroxylation increases with quinone concentration, (ii) the yield of hydroxy derivatives are matched by an equal yield of H_2O_2, (iii) on anaerobic photolysis, similar hydroxylated products along with semiquinone and quinol are obtained and (iv) at a fixed [D] and light intensity the rate of photohydroxylation is independent of pH in the range 2.5–10.5 but rises sharply for pH > 10, proposed two alternate schemes, D*/S and D*/D, depending on whether the excited quinone interacts with the solvent or with ground state quinone :

D*/S scheme:

$$D \xrightarrow{h\nu} {}^{1}D^{*} \longrightarrow {}^{3}D^{*} \xrightarrow{+H_2O/-H^{+}} DOH^{\cdot}$$
${}^{3}D^{*} \xrightarrow{OH^{-}} D+OH^{-}$; $DOH^{\cdot} \xrightarrow{+OH^{-}} D+OH^{-}$; $DOH^{\cdot} \xrightarrow{+D,\ -D^{\cdot-}} DOH^{\cdot}$
$$HO_2^{\cdot} + ROH \longleftarrow O_2DOH^{\cdot} \xleftarrow{O_2} DOH^{\cdot}$$

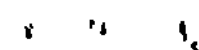
D*/D scheme:

$$ {}^{3}D^{*} + D \longrightarrow \{D^{\cdot+}\ D^{\cdot-}\} \xrightarrow[-D/-D^{\cdot-}]{OH^{-}} OH^{\cdot} \xrightarrow{D} DOH^{\cdot}$$
$\{D^{\cdot+}\ D^{\cdot-}\} \xrightarrow{OH^{-}} 2D+OH^{-}$; $\{D^{\cdot+}\ D^{\cdot-}\} \longrightarrow 2D$; $\{D^{\cdot+}\ D^{\cdot-}\} \xrightarrow{-D^{\cdot-}} D^{\cdot+}$; $D^{\cdot+} \xrightarrow{D^{\cdot-}} 2D$; $D^{\cdot+} \xrightarrow{+OH^{-}/-D;\ +H_2O/-H^{+}/-D} OH^{\cdot}$

In absence of oxygen, $2\,DOH^{\cdot} \rightarrow ROH+D+H_2O$
$$2\,D^{\cdot-} \rightarrow D^{-2}+D$$

The intermediacy of OH· in D*/D scheme was supported by the observed decrease in ROH yield in presence of some radical scavengers like formate, alcohol, etc.

Recently, from γ- and pulse radiolysis studies (where OH· is undoubtedly the hydroxylating agent) Clark and Stonehill[10] reported that the effect of photolysis and pH on the ROH yield is different in scavenger and γ-radiolysis eliminating the possibility of OH· radical involvement in photolysis. They

suggested a modification in the D*/D scheme as

$$\{D^{\cdot+}\,D^{\cdot-}\} \xrightarrow[-O^{\cdot-}]{\cdot OH^{-}} DOH^{\cdot}$$
$$\{D^{\cdot+}\,D^{\cdot-}\} \longrightarrow 2D$$
$$\{D^{\cdot+}\,D^{\cdot-}\} \xrightarrow{-O^{\cdot-}} D^{\cdot+}$$
$$D^{\cdot+} \xrightarrow{+OH^{-}\ |\ +H_2O/-H^{+}} DOH^{\cdot}$$
$$D^{\cdot+} \xrightarrow{+O^{\cdot-}} 2D$$

but still could not discriminate between the D*/D and D*/S primary steps.

The yield of ROH in the photolysis of D in anaerobic neutral solutions cannot be satisfactorily explained by the above schemes. Moreover, the formation of only β-ROH in alkaline medium and both α- and β-ROH in neutral and acid medium still remained unexplained. In the D*/S scheme, the formation of DOH^- as an adduct of OH^- and D in α-position and in β-position is unlikely. Assuming that the adduct is formed, it is yet difficult to justify the DOH^- reacting with D to yield DOH and $D^{\cdot-}$ in aerobic medium instead of DOH^- directly reacting with oxygen which would mean no production of $D^{\cdot-}$. There is, however, positive evidence of formation of $D^{\cdot-}$ on photolysis of D in aerobic medium.

Further, the D*/S scheme can not explain (i) the formation of hydroxy-benzoic acid when aqueous solution of D was irradiated in presence of benzoic acid and (ii) the formation of polyhydroxy derivatives of D on prolonged irradiation, though mono-hydroxy derivative has been reported[5] to be photoinactive.

The present work has been carried out with a view to establish the actual mechanism of the above photochemical reaction.

Experimental

Anthraquinone-2-Na-sulfonate (B.D.H.) was recrystallised five times from water in the dark and dried in a vacuum desiccator over fused $CaCl_2$. The purity of the compound was estimated by ion exchange process – an aqueous solution of the compound was passed through a cation-exchange resin (IRC-120 in H-form) column and the exchanged anthraquinone-2-sulfonic acid was estimated by titrating with a standard alkali solution.

The light source used was a medium pressure mercury vapour lamp (of M/S. Thermal Syndicate, U.K., model no. T/MS/577, 80 watts), mounted vertically on an optical bench. For isolating 366 nm radiation, the light after collimation was passed through a Chance's -O-O-glass filter and $CuSO_4$ solution [250 g/litre in 0.01 *N* H_2SO_4] of 1 cm path length. The irradiation cell (capacity 3 ml; path length 1 cm) was maintained at a constant temp of 29±0.1°. Light output was measured by ferrioxalate actinometry according to a modified method of Hatchard and Parker[11].

Aerobic photolysis:

Hydroxy-derivatives of anthraquinone-2-sulfonate were estimated according to the method of Clark and Stonehill[5]. For neutral and acidic solution the absorption at 476 and 491 nm were noted after alkalination to $pH > 11$. The extinction coefficients for α- and β-hydroxy derivatives at the above two wavelength are, $\epsilon^{\beta}_{476} = 3.6\times10^{3}$ lit. mol^{-1} cm^{-1}, $\epsilon^{\beta}_{491} = 3.4\times10^{3}$ lit. mol^{-1} cm^{-1} $\epsilon^{\alpha}_{476} = 5.09\times10^{3}$ lit. mol^{-1} cm^{-1} and $\epsilon^{\alpha}_{491} = 5.65\times10^{3}$ lit. mol^{-1} cm^{-1}, as reported by Clark and Stonehill[5]. For alkaline solution, it was assumed that only β-derivative was being formed and was estimated from the absorption of the photolysed solution at 476 nm. H_2O_2, produced on aerobic irradiation, was estimated by the method of Allen *et al*[12]. 1 ml of the photolysed solution was mixed with 1 ml of the reagent (a), [a solution of 1 g NaOH, 33 g KI and 0.1 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 ml water] and 1 ml of reagent (b), (10 g potassium hydrogen phthalate in 500 ml water). H_2O_2 was estimated from the absorption of the solution at 350 nm, after correcting for the absorptions of anthraquinone-sulfonate and its hydroxy derivatives at that wavelength.

Anaerobic photolysis:

The solutions were deoxygenated by bubbling high purity Argon (IOL AR 2 grade of Indian Oxygen Ltd.) through the solution for 1 hr before irradiation.

Irradiation under anaerobic condition of aqueous solution of anthraquinone-2-sulfonate in acidic or neutral medium produced an absorption maximum at 385 nm which disappeared on oxygenation. Similar irradiation in alkaline medium showed absorption maxima at 400 and 500 nm which disappeared on oxygenation leaving a broad band at 476 nm. The spectra of the photolysed solution under anaerobic medium and that after subsequent aeration were recorded with a Beckmann DU spectrophotometer. The difference of the two gave the spectra of the reduced species.

In order to identify the reduced product, D has been reduced with sodium dithionite under anaerobic medium both in acid and alkaline medium. A closed cell containing weighed amount of solid dithionite was thoroughly deoxygenated with high purity argon and then 3 ml of a solution of D (also deoxygenated) was added to it with a syringe. To produce semiquinone ($DH^{\cdot}$) and semiquinolate ($D^{\cdot-}$), ion the amount of dithionite taken was such that less than 50% reduction occurred. The spectra of quinol (DH_2) and quinolate (D^{-2}) ion produced by adding excess of dithionite were also recorded. Hydroxy derivatives produced on anaerobic irradiation were estimated from the oxygenated solution by the method used in the case of aerobic irradiation.

Determination of extinction coefficient of $DH^{\cdot}$: Though earlier workers[13] reported the extinction coefficient of $DH^{\cdot}$, they determined this value from the transient spectra recorded 20 μsec after pulse radiolysis of Ar-saturated solution of D at pH 4 (after subtraction of DOH and $D^{\cdot-}$ contribution) assuming that the ionisation equilibrium ($DH^{\cdot} \rightleftharpoons D^{\cdot-} + H^{+}$) is established very soon after the pulse. But it has been found from flash photolysis studies[14] that this ionisation equilibrium is attained not

before a few milliseconds which means that the determination may suffer from non-attainment of equilibrium, leading to an incorrect extinction coefficient.

In the present determination, the species DH· was produced by reducing Ar-saturated solution of D with dithionite in acid medium by the method mentioned earlier and its spectrum was recorded. The solution was then made alkaline by adding 0.3 ml alkali (previously deoxygenated), with the help of a syringe when DH· was converted to $D^{\cdot -}$ and the spectrum was recorded again. Using the extinction co-efficient of $D^{\cdot -}$ at 500 nm, previously determined by electrochemical reduction of D, the concentration of semiquinone has been determined and the extinction co-efficient of DH· at 385 nm was calculated (taking into consideration the absorption of D at 385 nm). The value is 5.55×10^{3} lit. $mol^{-1} cm^{-1}$, while the previously reported value is 1.2×10^{4}, apparently from the use of a lower value for the concentration of DH·.

Photolysis of anthraquinone-2-sulfonate in presence of formate and azide in anaerobic medium : Argon-saturated solutions of D (5×10^{-4} *M*) in water, containing various concentrations of sodium formate were irradiated and subsequently analysed for semiquinone and hydroxylated products. The results are tabulated in Table 3. Argon-saturated solution of D ($5 \times 10^{-4} M$) in presence of formate ($1 \times 10^{-1} M$) at different *p*H were also irradiated (Fig. 1).

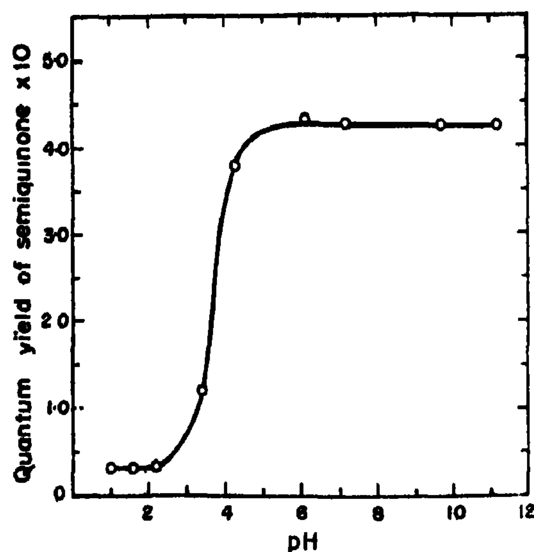


Fig. 1. Variation of quantum yield of semiquinone with *p*H in presence of formate.
[D] = $5 \times 10^{-4} M$; [formate] = $1 \times 10^{-1} M$

Argon-saturated solutions of D ($5 \times 10^{-4} M$) in water containing various concentration of azide were irradiated. The results are tabulated in Table 4.

Results and Discussion

Only mono-hydroxylated anthraquinone-2-sulfonate and hydrogen peroxide were identified as stable product after photolysis under aerobic condition. In acid and neutral medium both α- and β-hydroxy derivatives were formed, the ratio being 3 : 2 independent of irradiation time. In alkaline medium (at *p*H > 10) only β-hydroxy derivative was detected.

The quantum yields of hydroxy derivatives are matched by an equal yield of H_2O_2 (Table 1) and increases with (i) increase in initial concentration of D (Table 2) and (ii) decrease in irradiation time (Table 1). The dependence of quantum yield on initial concentration of D suggests the involvement of ground state quinone in the overall reaction. The yield is independent of *p*H in the range 2.5-10, but rises sharply for *p*H > 10

TABLE 1(a)—IRRADIATION IN NEUTRAL MEDIUM
[D] = $5 \times 10^{-4} M$

Time of irradiation in sec.	Aerobic medium		Anaerobic medium	
	ϕ_{ROH}	$\phi_{H_2O_2}$	ϕ_{ROH}	$\phi_{DH^\cdot}$
600	1.52×10^{-2}	1.42×10^{-2}		
900	1.49×10^{-2}	1.39×10^{-2}		
1200	1.47×10^{-2}	1.39×10^{-2}	2.74×10^{-3}	4.52×10^{-3}
1500	1.46×10^{-2}	1.37×10^{-2}	2.71×10^{-3}	4.49×10^{-3}

TABLE 1(b)—IRRADIATION IN ALKALINE MEDIUM
[OH^-] = 0.01*N* ; [D] = $5 \times 10^{-4} M$

Time of irradiation in sec.	Aerobic medium		Anaerobic medium	
	ϕ_{ROH}	$\phi_{H_2O_2}$	ϕ_{ROH}	$\phi_{D^{\cdot -}}$
600	4.23×10^{-2}	3.97×10^{-2}	2.02×10^{-2}	3.96×10^{-2}
900	3.90×10^{-2}	3.58×10^{-2}	1.73×10^{-2}	3.34×10^{-2}
1200	3.58×10^{-2}	3.27×10^{-2}	1.64×10^{-2}	3.23×10^{-2}
1500	3.30×10^{-2}	3.02×10^{-2}	1.50×10^{-2}	3.05×10^{-2}

Irradiation under anaerobic medium produces mono-hydroxy derivatives together with semiquinone/semiquinolate ion, thus suggesting the involvement of solvent molecule in the hydroxylation of D. No hydrogen peroxide could be detected when the estimation is carried out under anaerobic medium. With change of *p*H, similar distribution of isomeric hydroxy derivatives as with aerobic irradiation is observed. The quantum yield of semiquinone/semiquinolate ion is almost twice that of hydroxy derivatives and increases with (i) increase in initial concentration of D (Table 2) and (ii) decrease in irradiation time (Table 1).

For a fixed initial concentration of the quinone in alkaline medium the quantum yield of hydroxy derivative under anaerobic condition is slightly less than half of that under aerobic condition, while in acid and neutral medium the anaerobic yield is about one sixth of the aerobic yield. Results of Table 3 show that on irradiation of D in presence of formate (a known OH· radical scavenger) the yield of hydroxy derivatives decreases, while that of semiquinone/semiquinolate ion increases compared to that in absence of formate. With increase in formate concentration, the yield of hydroxylated product decreases (and above 10^{-2} *M* formate, no hydroxy product can be detected) with concurrent increase of semiquinone yield. If the formate had acted only

TABLE 2—VARIATION OF QUANTUM YIELDS WITH [D]

Concentration of D in moles/litre	Neutral medium		Alkaline medium ; $OH^- = 0.1\ N$		
			Aerobic medium	Anaerobic medium	
	ϕ_{ROH}	$\frac{\alpha\text{-ROH}}{\beta\text{-ROH}}$	ϕ_{ROH}	ϕ_{ROH}	$\phi_{D^{\cdot -}}$
5×10^{-3}	4.84×10^{-2}	1.52			
4×10^{-3}	4.57×10^{-2}	1.58	1.75×10^{-1}	8.57×10^{-2}	1.69×10^{-1}
3×10^{-3}	4.21×10^{-2}	1.54	1.58×10^{-1}	7.81×10^{-2}	1.53×10^{-1}
2×10^{-3}	3.63×10^{-2}	1.43	1.43×10^{-1}	6.95×10^{-2}	1.38×10^{-1}
1×10^{-3}	2.54×10^{-2}	1.44	9.41×10^{-2}	4.67×10^{-2}	9.26×10^{-2}
5×10^{-4}	1.51×10^{-2}	1.62	5.90×10^{-2}	2.92×10^{-2}	5.76×10^{-2}

TABLE 3—VARIATION OF QUANTUM YIELD OF SEMIQUINOLATE ION ($D^{\cdot -}$) AND HYDROXY DERIVATIVE OF D (ROH), ON PHOTOLYSIS OF ANTHRAQUINONE-2-SULFONATE SOLUTION ($5 \times 10^{-4} M$) AT $pH = 11.2$ WITH DIFFERENT CONCENTRATION OF NA-FORMATE (UNDER ANAEROBIC CONDITION)

Initial concentration of Na-formate in moles/litre	No. of light quanta absorbed per second	No. of molecules of ROH formed per second	No. of molecules of $D^{\cdot -}$ formed per second	Quantum yield of ROH ϕ_{ROH}	Quantum yield of $D^{\cdot -}$ $\phi_{D^{\cdot -}}$
8.0×10^{-1}	3.383×10^{15}	–*	1.948×10^{15}	—*	5.76×10^{-1}
4.0×10^{-1}	3.411×10^{15}	–	1.727×10^{15}	—	5.06×10^{-1}
1.0×10^{-1}	3.466×10^{15}	–	1.461×10^{15}	—	4.22×10^{-1}
5.0×10^{-2}	3.496×10^{15}	–	1.218×10^{15}	—	3.49×10^{-1}
2.0×10^{-2}	3.549×10^{15}	–	9.516×10^{14}	—	2.68×10^{-1}
1.0×10^{-2}	3.577×10^{15}	–	7.860×10^{14}	—	2.20×10^{-1}
5.0×10^{-3}	3.605×10^{15}	4.183×10^{13}	5.979×10^{14}	1.16×10^{-2}	1.66×10^{-1}
2.5×10^{-3}	3.605×10^{15}	6.074×10^{13}	4.650×10^{14}	1.68×10^{-2}	1.29×10^{-1}

*'—' indicates conc. below limit of detection.

as a scavenger of $OH^{\cdot}$ radical (a possible precursor of ROH yield) as suggested by Clark and Stonehill, the decrease of ROH yield in its presence would not have resulted in a concurrent increase of semiquinone yield. The lower yield of ROH may be due to higher reactivity of formate than water towards the intermediate which reacts with water producing ROH. This is further supported by the results in Fig. 1. The pK value of formic acid is 3.75. The results indicate that at and above pH 4.75, where it exists as $HCOO^-$, the quantum yield of semiquinone is appreciably higher compared to that below pH 3 where it exists exclusively in the undissociated HCOOH form, and in between pH 3 - 4.75 the yields increase with increase in pH due to increase of the ratio $HCOO^-/HCOOH$ in the solution.

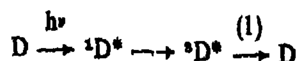
The variation of the yield of semiquinone with pH in presence of formate can be correlated with the observed dependence of ROH yield on pH in absence of any added substrate. In the pH range 2.5 - 10, where OH^- ion concentration is much less than that of quinone usually used ($10^{-3}M$), the yield is much lower because of the fact that undissociated H_2O participates in the reaction and hence pH has no effect on the yield of ROH in this region. Above pH 10, the yield of ROH and semiquinone increases with increase in pH, due to the reason that at OH^- concentration higher than $10^{-4}M$, this ion participates in the reaction and the yield increases due to its higher reactivity than H_2O.

Table 4 shows the variation of ROH and semiquinone yield with added NaN_3. In presence of NaN_3 both the ROH and semiquinone yield decreases and at higher concentration of azide no semiquinone as well as ROH formation is observed. This suggests that azide probably scavenges a common precursor of both ROH and semiquinone.

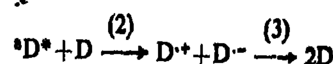
TABLE 4—QUANTUM YIELD OF ROH AND SEMIQUINONE ON IRRADIATION OF ANTHRAQUINONE-2-SULFONATE ($5 \times 10^{-4} M$) SOLUTION IN PRESENCE OF NaN_3 at pH 11.2

Concentration of NaN_3	Quantum yield of ROH	Quantum yield of $D^{\cdot -}$
$5 \times 10^{-3} M$	1.62×10^{-2}	3.08×10^{-2}
$1 \times 10^{-2} M$	6.67×10^{-3}	1.31×10^{-2}
$1 \times 10^{-1} M$	0	0

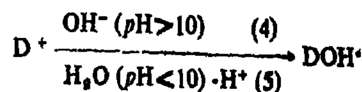
The D^*/S scheme, in addition to its draw-backs as discussed earlier, can not explain the higher reactivity of OH^- and $HCOO^-$ compared to H_2O and HCOOH and thus the possibility of its involvement is excluded. The D^*/D scheme, after modification by Clark and Stonehill, can explain the observed results qualitatively, but it fails to explain the observed variations of ROH yield and α-ROH/β-ROH ratio with pH. To account for these observations we suggest that D^+ must be reacting with OH^- at $pH > 10$ and at pH below 10, it reacts with H_2O molecule. The D^*/D scheme with modified steps (4) and (5) is given below :



$$D \xrightarrow{h\nu} {}^1D^* \longrightarrow {}^3D^* \xrightarrow{(1)} D$$



$${}^3D^* + D \xrightarrow{(2)} D^{\cdot +} + D^{\cdot -} \xrightarrow{(3)} 2D$$



$$D^{+} \xrightarrow[H_2O\ (pH<10)\ \cdot H^+\ (5)]{OH^-\ (pH>10)\quad (4)} DOH^{\cdot}$$

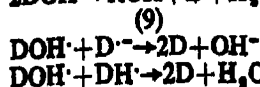


$$D^{\cdot -} + H^+ \rightleftharpoons DH^{\cdot}$$

In absence of oxygen

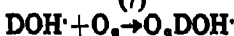


(8)
$2DOH^{\cdot} \rightarrow ROH + D + H_2O$

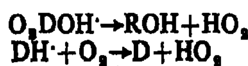


(9)
$DOH^{\cdot} + D^{\cdot -} \rightarrow 2D + OH^-$
$DOH^{\cdot} + DH^{\cdot} \rightarrow 2D + H_2O$

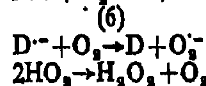
In presence of oxygen



(7)
$DOH^{\cdot} + O_2 \rightarrow O_2DOH^{\cdot}$

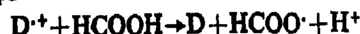


$O_2DOH^{\cdot} \rightarrow ROH + HO_2$
$DH^{\cdot} + O_2 \rightarrow D + HO_2$

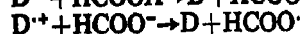


(6)
$D^{\cdot -} + O_2 \rightarrow D + O_2^{\cdot -}$
$2HO_2 \rightarrow H_2O_2 + O_2$

In presence of formate the reaction proceeds through the steps :



$D^{\cdot +} + HCOOH \rightarrow D + HCOO^{\cdot} + H^+$

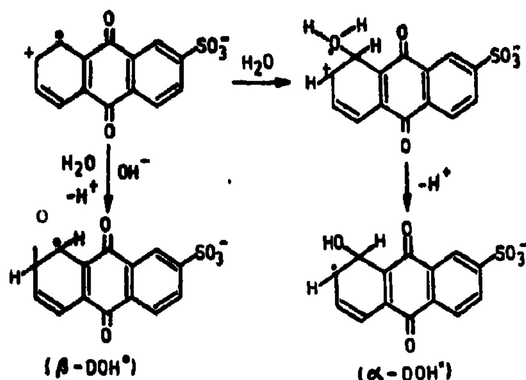


$D^{\cdot +} + HCOO^- \rightarrow D + HCOO^{\cdot}$

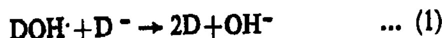


$D + HCOO^{\cdot} \rightarrow D^{\cdot -} + CO_2 + H^+$

The higher yield of ROH and/or semiquinone in presence of ionic species OH^-, $HCOO^-$ compared to that in presence of H_2O and HCOOH can be explained in terms of added electrostatic force between opposite charges. Formation of α- and β-ROH in neutral and acid medium and only β-ROH in alkaline medium is probably due to the reason that in alkaline medium OH^- attacks preferentially at the (+)ve centre while in acid and neutral medium, where the attacking agent is H_2O, it can attack both at the radical carbon or the (+)ve carbon as,



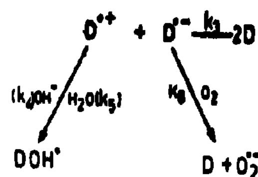
In alkaline medium the yield of ROH under anaerobic condition is always slightly less than half of the aerobic yield. This supports the bimolecular reaction of $DOH^{\cdot}$ in the former case. But in acid and neutral medium the anaerobic ROH yield is about six times less than the aerobic yield which is in agreement with the observation of Burchill *et al*[15]. These authors suggested that the reduced yield in anaerobic neutral solution is due to the preferential cross reaction between DOH and $D^{\cdot -}$ as



$$DOH^{\cdot} + D^{\cdot -} \rightarrow 2D + OH^- \quad \dots (1)$$

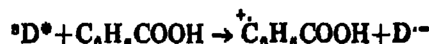
while in alkaline anaerobic solution similar cross reaction does not occur and mutual bimolecular reaction of $DOH^{\cdot}$ is the only path leading to ROH. Why the reaction (1) occurs only in acid and neutral medium (below *p*H 10) and not in alkaline medium is not clear. We suggest the following to explain the above results.

The higher yield of ROH in alkaline medium compared to neutral and acid medium implies that $k_4 > k_5$.

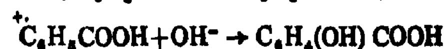


Again, the almost half yield of ROH in anaerobic condition compared to aerobic one (i.e. almost equal yield of DOH in both cases) suggests that $k_4 > k_8$. For acid and neutral medium, probably $k_8 < k_6$, so that in aerobic condition $DOH^{\cdot}$ (and ROH) yield is determined by the rate of oxidation of $D^{\cdot -}(k_6)$ and thus aerobic $DOH^{\cdot}$ yield will be higher than anaerobic $DOH^{\cdot}$ yield and the ratio of aerobic and anaerobic ROH yield will be greater than two.

The formation of hydroxy-benzoic acid on irradiation of aqueous solution of D in presence of benzoic acid can be explained by the proposed scheme, where the excited quinone presumably abstracts electron from benzoic acid as



$$^3D^* + C_6H_5COOH \rightarrow \overset{+\cdot}{C_6H_5}COOH + D^{\cdot -}$$



$$\overset{+\cdot}{C_6H_5}COOH + OH^- \rightarrow C_6H_4(OH)\,COOH$$

By applying steady state hypothesis to the various intermediates in the above proposed scheme, the following expressions are obtained. In oxygenated alkaline solution, we have

$$\frac{[D]}{\phi_{ROH}} = \frac{k_1(k_3+k_4[OH^-])}{k_3k_4[OH^-]} + \frac{k_3+k_4[OH^-]}{k_4[OH^-]}[D], \quad \dots (A)$$

In deoxygenated alkaline solution, the expression becomes

$$\frac{[D]}{\phi_{ROH}} = \frac{k_1k_x(k_3+k_4[OH^-])}{k_3k_4k_8[OH^-]} + \frac{k_x(k_3+k_4[OH^-])}{k_4k_8[OH^-]}[D] \quad \dots (B)$$

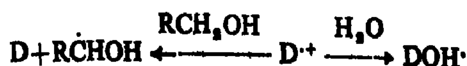
$$[k_x = k_8 + k_9]$$

In oxygenated neutral solution, it is

$$\frac{[D]}{\phi_{ROH}} = \frac{k_1(k_3+k_5)}{k_3k_5} + \frac{k_3+k_5}{k_5}[D] \quad \dots (C)$$

In accordance with (A), (B) and (C), $[D]/\phi_{ROH}$ is linear with [D] (at fixed $[OH^-]$ in alkaline medium) and intercept slope ratio (k_1/k_3) is independent of irradiation, *p*H, and presence of O_2 (Fig. 2).

Though it has been suggested that the well studied photo-oxidation of alcohol[9] by anthraquinone-2-sulfonate involves α-H-abstraction from the alcohol by the excited quinone, the possibility of involvement of a similar D^*/D mechanism ($D + D^* \rightarrow D^{\cdot +} + D^{\cdot -}$, $D^{\cdot +} + RCH_2OH \rightarrow R\dot{C}HOH + D$ ..) may also be considered to allow the formation of ROH as well as oxidation product of alcohol in aqueous alcohol media.



$$D + R\dot{C}HOH \xleftarrow{RCH_2OH} D^{\cdot +} \xrightarrow{H_2O} DOH^{\cdot}$$

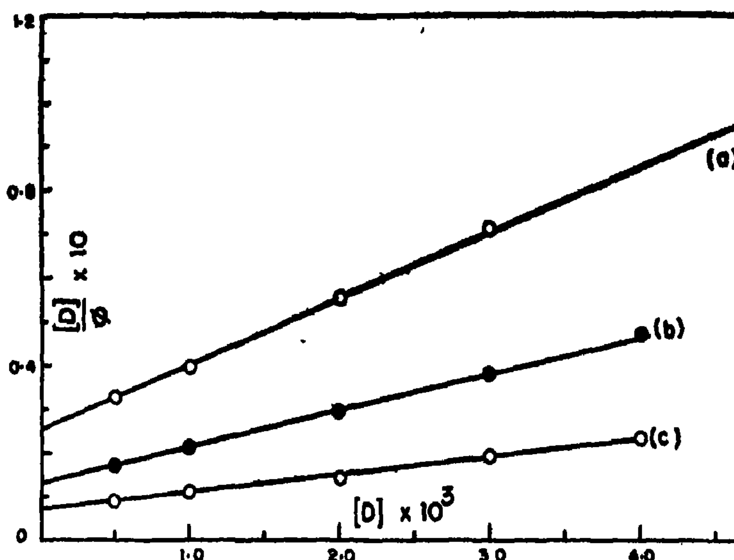


Fig. 2. Dependence of photohydroxylation yield on concentration of 'D': (a) neutral medium (aerobic), (b) alkaline medium (anaerobic), (c) alkaline medium (aerobic).

Indeed this can well explain the observed decrease in the rate of oxidation of alcohol in alkaline medium due to higher reactivity of OH^- than H_2O towards $D^{\cdot +}$.

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Ultrasonic Study of the Elastic Constants of Some Ancient and Mediaeval Indian Coins

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Using the ultrasonic pulse technique, elastic constants like the bulk modulus, shear modulus, Young modulus and Poisson's ratio, have been determined for Indian coins belonging to various periods of history. The results are discussed in the light of chemical composition, spectrographic analysis and the microstructural observations.

FOR the last several years, the senior author has been interested in the archaeological studies of Indian antiquities. Prakash and Rawat[1] published a monograph giving a detailed account of their results on the chemical analysis of some of the objects of interest found at Kausambi. Later, Prakash and Singh[2] reported their results on the chemical, spectrographical, microstructural studies of a large number of Indian coins from the earliest times. In a recent paper, Prakash and Murthy[3] have published their results on the heterogeneity of ancient Indian coins. In the present paper, an attempt has been made to calculate several elastic constants of the metals used in coinage during different historical periods using the ultrasonic pulse technique.

Experimental

The coin from the hoard is first cleansed by the usual methods and polished. For the ultrasonic pulse technique, the coin is suspended in an ordinary rectangular brass cell containing water, having two quartz crystals (serving as transducer and receiver) parallel to each other and fixed on the opposite walls. The technique uses a synchronizing generator (SG), time-based generator (TBG), wide band amplifier (WBA), detector (DA) and output amplifier (OPA) connected in sequence (Fig. 1). The oscillograph (OSC) and the output stage (OPS) are also

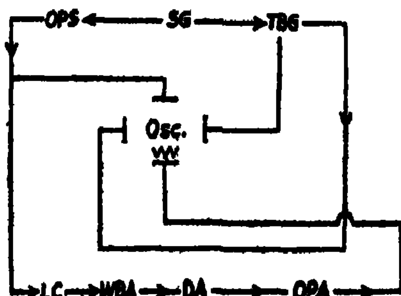


Fig. 1. Pulse technique.

shown in the figure. As the coin is rotated from the original direction (i.e. at right angles to the direction of the incoming ultrasonic waves) within 90°, two critical angles (θ_1 and θ_2) are obtained. When the coin is perpendicular to the direction of longitudinal waves, the waves are transmitted completely as longitudinal waves. As the angle between the direction of longitudinal waves and the coin is decreased from 90°, a point comes when there is no transmission of the longitudinal waves. This is our first critical angle (θ_1). The coin is continued to rotate till a second critical angle (θ_2) is obtained at which shear waves in the coin also cease to be transmitted. For the position beyond this critical angle, there will be no transmission of ultrasonic waves (provided the coin possesses a certain minimum size). Using these two critical angles, we have been able to calculate certain elastic constants for the metals of the coins.

Elasticity constants from the critical angles :

If V_L is the velocity of longitudinal waves in water (which is 1470 m/sec at 27°), V'_L the velocity of the longitudinal waves in the coin, and V'_S is the velocity of the shear waves in the coin, then the critical angles θ_1 and θ_2 are related as :

$$V'_L = V_L / \sin\theta_1$$
$$V'_S = V_L / \sin\theta_2$$

The bulk modulus K and Poisson's ratio σ are given by the expressions :

$$K = V'_L / V'_S$$
$$\sigma = (K^2 - 2)/2(K^2 - 1)$$

The Young modulus (E) and the shear modulus (F) are related to the Poisson's ratio and the density (ρ) of the coin as well as to each other by the following two expressions :

$$E = 2(1+\sigma)F$$
$$F = (V'_S)^2 . \rho$$

From Snell's law we know that

$$\sin\theta / V_L \pm \sin\theta_L / V'_L = \sin\theta_S / V'_S$$

where θ is the angle of incidence of longitudinal waves at the surface of the solid, and θ_L and θ_S are the angles of transmission of the longitudinal and shear waves in the solid, respectively.

Before starting our work on the old and ancient coins of India we studied, for reference, some modern coins for their elastic constants by the

pulse technique and Table 1 gives these results. The subsequent tables give our results on the punch-marked coins (*karshapanas*) belonging to about 300-200 B.C., Indo-Sasanian coins (550-700 A.D.), *Kushana* copper coins (25-425 A.D.), Oudh coins (1700 A.D.), Kashmir coins (100 A.D.), Yaudheya coins ; *Bahamani* coins (1358-1482 A.D.), coins of Shershah (1539-45 A.D.) and Islamshah (1545-53 A.D.) Mughal coins of Akbar (1556-1605), Jehangir (1605-27), Shahjahan (1627-58) and Aurangzeb (1658-1707), and some other miscellaneous coins (*Kausambi*, *Taxila*, *Zemisis*, *Chola* and *Lanky-bull*). The chemical and spectrographic analyses of these coins have been reported by us earlier[8].

Discussion

Perhaps, the earliest work on ancient coins was started by Klaproth near about 1815[4], followed by Bibra (1869) on bronzes and copper alloys of ancient times[5]. Since 1922, various attempts have been made by the Archaeological Survey of India to carry-out scientific investigations on ancient metal objects, including those found at the capital sites of Mohenjo-daro and Harappa. Analyses of ancient Indian bronzes were reported by C. H. Desch to the Sumerian Copper Committee and many of these were incorporated in Sir John H. Marshall's complete report on the archaeological investigation and M. S. Vats report on Harappa excavations[7].

TABLE 1—BULK MODULUS AND POISSON'S RATIO OF SOME MODERN COINS

Coin	θ_1 mean	θ_2 mean	V_L' m/sec	V_S' m/sec	K	σ
5 RF Franc, (1945)	11°30′	32°15′	7373.3	2754 8	2.672	0 4189
Penny, British, (1936)	18 22.5	47 45	4663	1986	2.3479	0.3316
Arab, (1900)	18 52.5	40 7.5	4544	2281	1.9921	0.3316
Heliana, (1952)	12 55	32 22.5	6576	2745	2.3956	0.3945
Franc, (1943)	13 7.5	34 45	6474	2579	2.5103	0.4057
Shilling, British, (1953)	17 00	35 22.5	5028	3862	1.3019	0.2195
Paisa, Indian, (1966)	18 7.5	35 37.5	4725	2524	1.8720	0.3004

TABLE 2—ELASTIC CONSTANTS OF SOME PUNCH-MARKED COINS (300-200 B.C.)

(Rectangular ; figures of animals, wheel etc. on reverse.)

	Weight (g)	Thickness (mm)	Density (ρ)	θ_1	θ_2	V_L' m/sec	V_S' m/sec	K	σ	$E \times 10^{11}$	$F \times 10^{11}$
1.	3.240	0 29	6.77	24°15′	47°45′	3579	1986	1.8021	0.2775	6.83	2.670
2.	3.260	0 28	6.64	12 52.5	34 45	6597	2579	2.5580	0.4098	12.45	4.416
3.	3.215	0.26	6.89	15 52.5	48 15	5374	1970	2.7279	0.4223	7.61	2 674

TABLE 3—ELASTIC CONSTANTS OF INDO SASANIAN COINS (550-700 A D.)

	Weight (g)	Thickness (mm)	Density (ρ)	θ_1	θ_2	V_L' m/sec	V_S' m/sec	K	σ	$E \times 10^{11}$	$F \times 10^{11}$
1.	3 550	0 36	6.53	17° 7.5′	45°00′	4992	2079	2 4012	0.3951	7.87	2.822
2.	3.716	0 38	6.84	21 22.5	44 30	4033	2097	1.9232	0.3147	7.91	3.008

TABLE 4—ELASTIC CONSTANTS OF *Kushana* COPPER COINS (25-425 A.D.) AND OUDH COINS (1700 A.D.)

(circular with the portrait of the king on the obverse and a figure of certain deity on the reverse)

	Weight (g)	Thickness (mm)	Density (ρ)	θ_1	θ_2	V_L' m/sec	V_S' m/sec	K	σ	$E \times 10^{11}$	$F \times 10^{11}$
						Kushana					
1.	14.905	0.35	8.61	16°45′	3δ° 7.5′	5101	2381	2.1424	0.3607	13.28	4.881
2.	13.995	0 28	8.22	19 15	34 45	4459	2579	1.7290	0.2487	13.63	5.459
3.	12.335	0 35	7.79	17 52.5	42 00	4789	2197	2.1798	0 3667	10.28	3.760
4.	15 995	0.40	7.95	16 52.5	45 00	5064	2079	2.4358	0.3986	9.61	3.436
5.	14.897	0.30	8.17	18 30	43 45	4633	2126	2.1792	0.3666	10.09	3.693
						Oudh					
1.	10.465	0.41	10.43	41 7.5	56 45	2235	1758	1.2713	0.3114	4.44	3.224
2.	10.723	0.39	9.89	16 00	41 22.5	5333	2224	2.3979	0.3947	13.65	4.892
3.	11.06	0 41	10.52	19 15	61 37.5	4459	1671	2.6685	0.4183	8.33	2.937
						Kashmir					
1.	7.612	0.41	7.53	17 30	34 30	4888	2595	1.8836	0.3038	13.22	5.071
2.	6.852	0.40	7.86	19 00	36 00	4515	2501	1.8053	0.2787	12.57	4.916
						Yaudheya					
1.	11.190	0.41	9.55	15 30	35 30	5501	2531	2.1734	0.3657	16.71	6.118
2.	5.154	0.40	9.38	17 75	41 45	4992	2208	2.2609	0.3784	12.61	4.375

TABLE 5—ELASTIC CONSTANTS OF COINS OF BAHAMANI KINGS, SHERSHAH AND MUGHAL EMPERORS (1358 TO 1707 A.D.)

Bahamani Kings : Coins 1 and 2 : Bin Mahmud Shah (1358-73) ; Coin 3 · Humayum Shah (1457-61) ; Coin 4 : Muhammad III (1463-82) ; Coins 5 and 6 · Shershah (1539-45) ; Coins 7 and 8 Islamshah (1545-53) ; Mughal coins : Coins 9-12 : Akbar (1556-605) ; Coin 13 Jehangir (1605-27), Coins 14 and 15 : Shahjahan (1627-58), and Coins 16-21 : Aurangzeb (1658-1707). (Circular ; King's portrait on the obverse and the name of the mint on the reverse)

	Weight (g)	Thickness (mm)	Density	θ_1	θ_2	V_L'	V_S'	K	σ	$E \times 10^{11}$	$F \times 10^{11}$
					Bahamani						
1.	15.650	0 58	7 97	17°30′	38°52.5′	4889	2342	2.0875	0.3511	11 81	4.372
2.	16 357	0 50	8 46	17 7 5	37 45	4992	2401	2.0791	0.3495	13.16	4 877
3.	16 990	0 60	8.37	16 30	37 52.5	5176	2394	2 1621	0.3639	13 08	4 797
4.	19.735	0 60	8.35	18 15	39 22.5	4694	2317	2.0259	0 3389	12.01	4 483
					Shershah						
5.	20.370	0 61	8 41	16 52 5	37 52 5	5064	2394	2 1153	0 3561	13.07	4.820
6.	20.145	0.70	8.51	17 7.5	37 52 5	4992	2394	2 0852	0.3507	13.17	4 877
					Islamshah						
7.	20.490	0 70	8.42	16 15	37 15	5253	2429	2.1626	0 3640	13 55	4.968
8.	11.230	0.39	10.18	21 45	58 00	3967	1733	2 2891	0.3821	8 45	3.057
					Akbar						
9.	19.070	0.50	8 37	19 22.5	40 15	4431	2275	1.9477	0.3210	11 45	4 332
10.	20.005	0.40	8 36	18 15	38 00	4694	2388	1 9657	0.3254	12.64	4 767
11.	18.730	0.50	8.37	19 22.5	40 15	4431	2275	1 9477	0 3210	11 45	4.332
12.	11.287	0.39	10.33	19 15	59 00	4459	1715	2.6000	0.4132	8.59	3.038
					Jehangir						
13.	11.225	0.30	10.37	20 7.5	58 22 5	4272	1726	2.4751	0.4025	8.67	3.089
					Shahjahan						
14.	11.230	0.34	10.36	24 22 5	53 22 5	3562	1832	1 9443	0.3202	9 18	3.477
15.	10.085	0.32	10.43	19 7.5	52 30	4487	1853	2.4215	0.3972	10.01	3.581
					Aurangzeb						
16.	20.770	0.66	8.29	17 30	41 15	4889	2230	2 1924	0 3687	11 29	4.123
17.	20.301	0.62	8.46	14 52.5	36 45	5726	2457	2 3305	0 3872	14 17	5 107
18.	20.765	0.60	8 40	17 15	38 30	4957	2361	2 0995	0.3532	12 67	4.682
19.	20.680	0.69	8 44	17 53 5	39 45	4789	2299	2 0831	0 3503	12.05	4.461
20.	11.325	0.32	10.43	16 30	50 00	5176	1919	3 0099	0 4380	11 05	3.841
21.	11.261	0.33	10.39	20 37.5	59 45	4173	1702	2 4518	0 4002	8 43	3.010

TABLE 6—ELASTIC CONSTANTS OF MISCELLANEOUS OLD COINS

Weight (g)	Thickness (mm)	Density (ρ)	θ_1	θ_2	V_L' m/sec	V_S' m/sec	K	σ	$E \times 10^{11}$	$F \times 10^{11}$
					Kausambi					
5.640	0.32	6.63	16°45′	36°15′	5104	2487	3.0522	0.3440	11.02	4.101
					Taxila					
9.704	0.42	7.83	17 30	36 15	4956	2487	1.9968	0.3326	12.90	4.842
					Zemisis					
4.690	0.36	7.90	19 15	39 52 ·	4461	2293	1.9454	0.3205	10.97	4.154
					Chola					
8 279	0.39	8.12	20 00	42 22	4298	2183	1 9688	0 3261	10.26	3.870
					Lanky-bull					
5.675	0.37	6.54	17 80	35 45	4936	2515	1 9825	0.3293	11.00	4.137

Prof. E. R. Caley's work on Greek and Roman coins evoked our interest in the archaeological chemistry of ancient Indian coins, and our results have been incorporated in a comprehensive monograph[8]. Birbal Sahni published in 1945 a memoir on the techniques of casting coins in ancient India on behalf of the Numismatic Society of India[9]. Most of the techniques utilised for the study of the ancient coins are destructive in the sense that a few grains of the material has to be knocked out of the coin, and hence the museums are always reluctant in sparing their valuable collections. In search of a non-destructive method, we have taken recourse to the ultrasonic pulse technique. The earliest coins studied in the present project were the punch-marked coins of about 200 B. C., consisting of a metal with density (6.64-6.89) and thickness near about 0.28 mm. The most representative specimens are available

from Taxila hoard, Bodenayakanur hoard and Paila hoard, and also from Andhra Pradesh. Among the commonest coins of ancient India are the unscribed cast copper pieces, square, round or rectangular in shape, having symbols in relief (like a tree in railing, hollow cross, crescented hill or elephant). They are usually found on sites which yield punch-marked silver coins. From our analysis, we find that the composition of the punch-marked rectangular silver coins in terms of silver and copper is

	Coin 1	Coin 2	Coin 3	Coin 4
Ag	65.97	88.46	91.72	20.4
Cu	32.21	9.60	7.32	77.23

The punch-marked copper coins we studied had the following compositions: Cu, 89-91; Pb, 5.94; Sn, 0.77-2.27; Fe, 1.44-5.1%. Punch-marked copper coins are much rarer than the punch-marked silver coins.

We have earlier given[3] the detailed chemical compositions and the results of the spectrographic analysis and microstructures of the coins. In this paper, we present our results on the elastic properties of the coins. For reference, we are giving here the bulkmodulus (K), Poisson's ratio (σ), Young modulus (E) and shear modulus (F) for the pure coinage metals.

	E $\times 10^{11}$	F $\times 10^{11}$	σ	K	Density
Copper	12.98	4.83	0.343	1.378	8.9
Silver	8.27	3.03	0.367	1.036	10.5
Lead	1.61	0.559	0.44	0.458	11.34
Iron, soft	21.14	8.16	0.293	1.698	—
Iron, cast	15.23	6.0	0.27	1.095	7.9
Tin	4.99	1.84	0.357	0.582	5.77 (α) 7.29 (β)
Zinc	10.84	4.34	0.249	0.72	7.1
Brass (Cu 30, Zn 70)	10.06	3.73	0.350	1.118	—

Indo-Sasanian coins are circular, with the average composition Ag, 15; Cu, 82; Pb, 0.84%. Some of them are poorer in silver, as low as 4.5%. Their elastic constants are given in Table 3. *Kushana* coins are of a wide period (25-425 A.D.); they are circular, with a royal figure on the obverse and a deity on the reverse. Their density is of the range 8.17-8.61. Analysis of a large number of *Kushana* coins with densities ranging between 7.79 and 8.61, and the chemical composition: Cu, 96-99 with small quantities of sulphur (0.69-1.23); iron from traces to 4.79% and with traces of nickel and calcium have been carried out. The elastic constants tabulated in Table 4 are compatible with the microstructure which consists of polyhedral grains of a single solid solution, showing lots of twin crystals. Under the microscope, some of the grains appear dark brown and some light brown. This difference in shade was discussed in an earlier publication[3]. The metal is quite homogeneized indicating that either the coin was cold-worked and reheated to a high temperature where a fairly good amount of recrystallization took place, or it was worked at a quite high temperature.

The next coins we studied were three centuries old (1700 A.D.). belonging to the rulers of Oudh. These coins are circular with density 9.8-10.4. Their elastic constants are also given in Table 4. This table also includes the measurements on Kashmir coins of an early period (100 A.D.) and the Yaudheya coins. The Yaudheya are known for their past history. The *sutras* of *Panini* (5th century B.C.) mention of them. They constituted a sturdy race of warriors. Sahni referred to their coins and minting moulds, and these coins have also been described by Swami Omananda in his monograph[9]. We could get two Yaudheya coins for our present study with densities 9.55 and 9.38.

The other coins that we have studied belong to the Muslim period with considerably developed technique of minting and metallurgy, the Bahamani coins of Karnataka (1358-1482 A.D.), Shershah coins and the coins of Mughal emperors. In the last table, we have included our measurements on some miscellaneous coins we could procure, belonging to the sites of *Kausambi* and *Taxila*, a coin of *Zemesis*, and of *Chola* family and a *Lanky-bull* coin. The last one has been so nicknamed from its having a mythical animal (partly a horse and partly a bull) on the obverse, and a tree in railing, a wheel, arched hill, or a swastika on the reverse[8,8]. The coin has small amount of tin and a good quantity of lead which could preserve it against the hazards of environments. Our analysis gave for the coin the following composition: Sn, 8.53-9.62; Cu, 89; Pb, 1.02-1.17; Fe, 0.32-0.41; Ni, 0.19-0.26; S, 0.24-0.27%.

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Kinetics of the Acid Catalysed Hydrolysis of Formamide in Binary-Aqueous Mixtures

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The kinetics of acid hydrolysis of formamide have been studied in binary aqueous mixtures with acetone, dioxan, 2-propanol and dimethylsulphoxide. The dipolar aprotic and non-hydrogen bond donor solvents like dioxan and acetone have a rate enhancing effect On the other hand protic solvents like alcohols, which can act both as hydrogen bond donor and acceptor, exert a rate decreasing effect DMSO, although a dipolar aprotic non-hydrogen bond donor solvent, has a rate decreasing effect possibly due to its strong interaction with hydrogen ions and association with water molecules.

THE kinetics studies in binary-aqueous mixtures have revealed that the effects of non aqueous component on the rate are generally complicated and not amenable to easy explanation in terms of the dielectric properties of the medium[1,2]. It is now recognised that the reorganisation of the solvent surrounding the reactants in the activation process, has a profound influence on the reaction rates. The addition of the cosolvent influences such a reorganisation and it cannot be treated as a mere diluent of water modifying its dielectric properties only[1,2]. Blandamer and Burgess[1] have discussed the interrelation of thermodynamic and structural properties of binary aqueous mixtures and the kinetic rate effects. In order to probe into such an interrelation, it was decided to study the acid hydrolysis of formamide in diverse solvents such as dioxan, acetone, dimethylsulphoxide (DMSO) and 2-propanol. Previously, this reaction has been studied in alkanols[3,4] and in dioxan[5].

In this study an attempt has been made to compare and correlate the kinetic effects of various solvents on the rate with their properties.

Experimental

Formamide (Koch-Light, A.R.), 1,4-Dioxan (Merck, extra pure), acetone (B.D.H., AnalaR), dimethylsulphoxide (Reidel, prosynth) and 2-propanol (S. Merck, L.R.) were used. All other chemicals were of reagent grade. The experiments were conducted in stoppered conical flasks immersed in water-bath at a desired temperature ($\pm 0.1°$). The reaction was initiated by mixing temperature equilibrated solution of formamide with temperature equilibrated mixture of hydrochloric acid and other chemicals. Aliquots were withdrawn from the reaction mixture after suitable intervals of time and analysed for ammonium ions, one of the reaction products, by formol titration method[6]. The duplicate rate measurements were reproducible within $\pm 5\%$.

Results

For studying the solvent effect, acetone, dioxan, DMSO and 2-propanol were used as cosolvent. The kinetics were studied by varying the percentage of nonaqueous cosolvent from 10 to 80% in binary-aqueous mixtures. The concentration of formamide and HCl were held constant at $0.5M$ each. The second order rate constants, k_2, were obtained using appropriate integrated rate equation in accordance with the rate law,

$$\text{Rate} = k_2 [HCONH_2][H^+] \quad (1)$$

The results are given in Table 1

TABLE 1—SECOND ORDER RATE CONSTANTS (k_2, $M^{-1}sec^{-1}$) FOR ACID HYDROLYSIS OF FORMAMIDE IN DIFFERENT AQUEOUS MIXTURES

Dioxan (40°)		Acetone (40°)		DMSO (40°)		2-Propanol (30°)	
% (v/v)	10^4k_2	% (v/v)	10^4k_2	% (v/v)	10^4k_2	% (v/v)	10^4k_2
0	6.9	0	6.9	0	6.9	0	2.70
20	6.8	20	6.8	20	6.5	10	2.42
40	6.8	40	6.7	40	6.1	15	2.25
60	7.5	50	6.8	60	4.3	20	2.25
80	12.3	60	7.1	80	2.15	30	2.00
		80	11.8			40	1.55
						50	1.40
						60	1.30
						80	1.22

A perusal of the kinetics results shows that in case of acetone and dioxan increasing amount of these solvents upto 40-50% in the aqueous mixtures had no effect on the rate. Thereafter the rate increases sharply. Earlier workers[4] have noted a slightly larger decrease in rate in dioxan-water mixtures followed by increase in rate above 50% dioxan-water compositions. The small decrease observed in the present study in the 0-50% range in both solvents is well within the experimental uncertainty of the present rate measurements and therefore does not appear to be significant.

In case of DMSO and 2-propanol the rate decreases continuously with the increase of their percentage composition in binary aqueous mixtures. For 2-propanol similar results have been noted by other workers too[3,4].

Discussion

In many cases the study of the solvent effect has been used as a diagonstic tool in deciding between A-1 and A-2 mechanism or in general between dissociative and associative mechanisms[9-11]. It has been argued[9] that the solvent effects are in general small for A-2 mechanisms. A perusal of kinetics results for different solvent systems (Table 1) shows that in all cases the variation in the values of the rate constants is within a factor of 4 although the solvent composition has been varied over a wide range. Similar kinetic behaviour have been noted by other workers also[3,4]. This clearly establishes a small effect of solvent composition on rate and is in conformity with the A-2 mechanism accepted for amide hydrolysis.

The correlation of solvent effect with mechanism is a ticklish problem and is, in general, dominated more by exceptions than rules. This is particularly true of amide hydrolysis because of the following two step mechanism :



$$RCONH_2 + H^+ \rightleftharpoons RCONH_3^+ \quad .. (2)$$



$$RCONH_3^+ + H_2O \longrightarrow RCOOH + NH_4^+ \quad ... (3)$$

How a particular solvent will affect each step is difficult to discern and what is experimentally observed is the net effect. On the face of it, since the reaction is between an ion and a neutral molecule[12], the rate should increase with the increase in the proportion of the less polar component in the reaction mixture. This is borne out only for acetone and dioxan and that too in the range of 50-80% (v/v) organic component. For others, the rate is found to decrease. For ion-dipole reactions, the present reaction being an example, the plot[12,13] of log k_D and 1/D is expected to be straight line where k_D is the rate constant in a medium of dielectric constant D. Such plots were non-linear for all the solvents studied and in no case a straight line was obtained. When the effect of dielectric constant for all the solvents studied including those by earlier workers, is compared, the dielectric constant as a principal source of solvent effects is ruled out as in all the cases the dielectric constant of the binary mixtures decreases with increasing organic cosolvent.

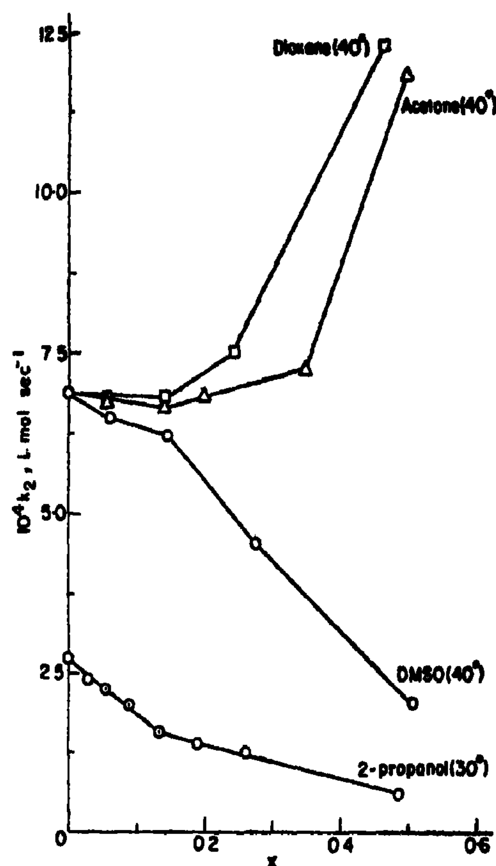


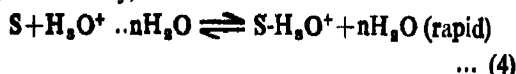
Fig. 1. The variation of second order rate constant, k_2, with the mole fraction, x of organic cosolvent in the acid hydrolysis of formamide

Fig. 1 shows the variation in rate constant, k_2, with mole fraction, x, of the organic component of the reaction mixture. In case of acetone, dioxan, DMSO and 2-propanol the rate is seen to change anomalously at the x values of 0.30, 0.15, 0.12 and 0.15 respectively. On the basis of thermodynamic functions of state, binary aqueous mixtures have been classified as typically aqueous (TA) and typically non-aqueous (TNA)[1]. TA mixtures are characterised by entropy controlled mixing while TNA mixtures by enthalpy controlled mixing. In TA mixtures, e.g., acetone-water, alcohol-water etc., as the mole fraction of cosolvent is increased it exerts a water structure forming action, the solvent co-spheres around each solute starts overlapping mutually enhancing water-water interactions. As more cosolvent is added and as soon as the mole fraction exceeds a particular value, x^*, there is insufficient water to maintain a three dimensional hydrogen bonded net work of water molecules and localised attempts to maintain this net work result in concentration fluctuations and the effect is maximal at a particular mole fraction x^{**}. The values of x^* and x^{**} are reported[1] to be 0.06 and 0.18 for 2-propanol and 0.06 and 0.35 for acetone at 25°. It has been said that these values provide a useful

sign post in effects on kinetic data and they are expected to undergo an anomalous change in these x-ranges. In conformity with the predicted kinetic rate effects the mole fractions (Fig. 1) at which the rates in different media change abruptly coincide remarkably with x^* and x^{**} values[1].

The values for the variation of k_2 with mole fraction for DMSO fall on two straight lines. One line lies in the x range of 0 to 0.15 and the other in the range of 0.15 to 0.5, the decrease in rate with increase of x being sharper in the second range. It is interesting to point out that the analysis of kinetics results of the hydrolysis of acetals in DMSO-water mixtures has shown[1,14] that the kinetic behaviour is different in the ranges $0<x<0.3$ and $0.3<x<0.45$. This is fairly in agreement with the observations made in the present work.

The acid hydrolysis of amides is assumed to involve the hydrogen bond equilibrium as in (4) and (5). Evidently, the



$$S+H_3O^+ \cdot\cdot nH_2O \rightleftharpoons S\text{-}H_3O^+ + nH_2O \text{ (rapid)} \quad \dots (4)$$



$$S \cdot\cdot H_3O^+ + H_2O \longrightarrow \text{products (slow)} \quad \dots (5)$$

ability of a solvent to partake in hydrogen bond formation is likely to influence the rate pattern in binary aqueous mixtures. DMSO and alcohols both are able to form strong hydrogen bonds but the basic difference between them is that while the former is only a hydrogen bond acceptor, the latter acts as donor and acceptor both and therefore the rate effects in the binary mixtures containing alcohols are expected to be more complicated. Indeed the rate constants for the acid hydrolysis of formamide pass through a minimum as the percentage of ethanol, 1-propanol and 2-methyl, 2-propanol is increased[3,4]. 2-Propanol appears to be an exception to this trend as neither we nor earlier workers[3,4] found any minimum in its rate pattern. Based on the fact that a large amount of heat is evolved when DMSO and water are mixed and that the viscosity isotherm passes through a maximum, it is believed that there is a strong association between water and DMSO due to hydrogen bonding[17]. It is known that the amount of free water decreases as the mole fraction of DMSO increases. In fact in the region $0.3<x<0.45$, the properties of the system are dominated by an associated species, H_2O : DMSO (2 : 1). In the present work it is this region in which the DMSO has a severe rate decreasing effect. Thus the effect of increasing DMSO in part may be due to decrease in free water concentration necessary for participation in step (2). The effect of DMSO can be explained in one more way. It is known that its basicity is comparable to that of water, and HCl has been found to be fully ionised in it[18,19]. Dehn, Gutman, Kirch and Schober[18] have shown that proton is more strongly bound to DMSO than water. It is thus possible that by tucking away hydrogen ions, DMSO can bring out the decrease in rate by shifting the equilibrium step (2) to the left. This also follows from the results of Tomilla and Musto[17] who found DMSO to decrease the protonation of certain indicators.

Dioxan and acetone both are hydrogen bond acceptor, the former being stronger than the latter. However, in one respect, dioxan is different from alcohols and DMSO. While the latter solvents exert a water-water structure forming action, the former is reported to be structure breaking[1]. This important difference in property may be a reason for rate enhancing effect of dioxan in the acid hydrolysis of amides. In line with the results of the present study, the dioxan and acetone are reported to increase the rate of the acid hydrolysis of γ-hydroxybutyeramide also[15].

The results obtained in the present work can be explained using another approach also. Using phenomenon of solvation of reactants and transition state, Pocker[16,20] has rationalised that the rate should increase with the decrease in polarity of solvent On this basis, the rate should increase in acetone and dioxan mixtures as is found in the present study. For ion-dipolar molecule reactions the rate is predicted to increase from protic solvents like water and alcohols to dipolar aprotic solvents like dioxan and acetone[16]. This is based on the relative solvating power of two media, the protic solvents being more solvating than aprotic ones[16]. Several examples of reactions of this charge type are known[16] in which the rate increases with decrease in the solvating power of the medium because the solvation energy of the smaller reactant ion, as in steps (2) and (3), is larger than the larger transition state ion causing an increase in the energy of activation in the stronger solvating media and hence the slower reaction rate.

In summary, the following conclusions may be drawn. The dipolar aprotic and non hydrogen bond donor solvents like dioxan and acetone increase the rate while protic solvents like alcohols decrease the rate DMSO, although a dipolar aprotic solvent, decreases the rate and this could be due to its strong interaction with H^+ and association with water molecules

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Physico-chemical Studies on Phosphorylation

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Cryoscopic, ebullioscopic, conductometric and *p*H determinations were carried out of orthophosphoric acid alone and mixed with adenine, adenosine, creatine, glycine, asparagine, methionine, glutamic acid, urea, glucose and sucrose The results indicate that mono-molecular complexes are formed by the interaction of phosphoric acid with purines, creatine and aminoacids in absence of enzymes and these complexes are stable even in the boiling solution.

IVANOV[1] showed that intact yeast converts phosphate to organic esters. Subsequently, various sugar-phosphates were identified as intermediates in the breakdown of starch and glycogen. There exists a mechanism within the cells, whereby the free energy available from oxidation reactions are utilized to drive endergonic processes. This is accomplished by trapping this energy through the formation of phosphate compounds of high energy content. ATP and phosphocreatine, containing "energy-rich" phosphate bond as named by Lipmann[6], play important role in the energy transformation in living tissues as stated by Lohman[7]. Formation of the above compounds in animal body is aided by enzymes. In the present investigation an attempt has been made to find out a physico-chemical basis of the phenomenon of phosphorylation in absence of enzymes.

Experimental

Reagent and chemicals: Adenine (Genatosan Ltd., Loughborough), Adenosine, (Hoffmann-La Roche, Basle), creatine, glycine, l-asparagine, dl-methionine, glutamic acid, urea, glucose, sucrose all B. D. H. AnalaR, phosphoric acid, (E Merck, AnalaR, sp. gr. 1.75) were used in these studies.

Phosphoric acid solution was standardised by estimating P_2O_5 by standard method[8]. Calculated amounts of nitrogenous compounds and carbohydrates were carefully added to 25 ml of standard H_3PO_4 solution in a 50 ml volumetric flask and the solution was made upto the mark with triple distilled water. The total volume of the mixture was 50 ml in every case.

Apparatus: Freezing-points and boiling-points of the solutions were determined with the help of a Beckmann thermometer. Conductivity was determined by Kohlrausch slide wire (Cat. No. 4258, Leeds & Northrup Philadelpia). A thermostat, fitted with a mercury-toluene thermoregulator, was used to maintain a constant temperature of 30° for measurement of conductivity of solutions. *p*H was measured by Beckman Glass Electrode *p*H Meter Model H-2.

Degree of association was calculated by applying the equation:

$$\alpha = \frac{dt - do}{dt\left(1 - \frac{1}{n}\right)}$$

Stability constant was calculated by applying the equation of Bjerrum, Schwarzenbach and Sillen[9] for monomolecular complexes:

$$K_{ML} = \frac{ML}{[M][L]}$$

$$K \text{ (stability constant)} = \frac{\alpha/10}{\left(0.1 - \frac{\alpha}{10}\right)\left(0.1 - \frac{\alpha}{10}\right)}$$

concentration of each reactant being $0.1M$.

Results and Discussion

The experimental results recorded in Table 1 show that when adenine or adenosine is added to H_3PO_4 the depression of freezing-point of the mixture is much smaller than the sum of the freezing-point depressions of the constituents. Further, if a calculated amount of glucose is added to the adenine H_3PO_4 or adenosine H_3PO_4 mixture, glucose depresses the freezing-point of the mixture to that extent it would, if dissolved in water alone. It is interesting to note that the degree of association, when 0.025 M adenine or adenosine is added to 0.1 M H_3PO_4, is the same and is 0.160. Moreover, the value of degree of association and also the stability constant is maximum when H_3PO_4 and adenosine are present in the solution in 1 : 1 ratio.

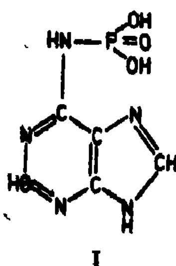
The essential difference between adenine and adenosine is that the latter contains a pentose conjugated in glycosidic linkage from carbon-1 of the sugar to nitrogen in 9 position. Adenine is soluble only to the extent of 0.025 M in 0.1 M H_3PO_4 whereas adenosine can dissolve in 0.1 M H_3PO_4 to the extent of 0.1 M. The greater solubility of adenosine in H_3PO_4 may be due to the pentose in the molecule. It has been stated[10] that the energy obtained from alcoholic fermentation of glucose can produce 4 high energy phosphate bonds whereas the complete oxidation of glucose, as in respiration, can produce 30 to 40 energy rich

TABLE 1

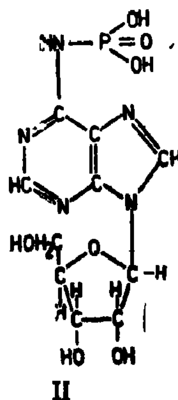
Solutions containing 0.1*M* H_3PO_4 and	Freezing-point depression of the mixture		Degree of association	Stability constant	Boiling-point elevation of the mixture		Degree of association	Stability constant
	Calcd.	Obsd.			Calcd.	Obsd.		
0.025 *M* adenine	0.281	0.245	0.160	–	0.073	0.065	0.136	–
0.025 *M* adenine + 0.05 *M* glucose	0.374	0.340	0.106	–	–	–	–	–
0.025 *M* adenosine	0.281	0.245	0.160	–	0.073	0.065	0.136	–
0.05 *M* adenosine	0.327	0.255	0.330	–	0.086	0.070	0.279	–
0.1 *M* adenosine	0.419	0.295	0.596	36.51	0.112	0.080	0.571	31.02
0.1 *M* adenosine + 0.1 *M* glucose	0.604	0.480	0.308	–	–	–	–	–
0.05 *M* creatine	0.327	0.280	0.215	–	0.086	0.075	0.192	–
0.1 *M* creatine	0.419	0.325	0.449	14.79	0.112	0.090	0.393	10.66
0.1 *M* creatine + 0.1 *M* glucose	0.604	0.510	0.233	–	–	–	–	–
0.05 *M* glycine	0.328	0.295	0.151	–	0.086	0.080	0.104	–
0.1 *M* glycine	0.420	0.355	0.309	6.66	0.112	0.095	0.304	6.27
0.2 *M* glycine	0.605	0.515	0.223	–	0.164	0.140	0.219	–
0.3 *M* glycine	0.790	0.685	0.177	–	–	–	–	–
0.05 *M* asparagine	0.327	0.285	0.192	–	0.086	0.080	0.104	–
0.1 *M* asparagine	0.419	0.335	0.401	11.56	0.112	0.090	0.393	10.66
0.2 *M* asparagine	0.603	0.490	0.280	–	0.164	0.135	0.265	–
0.05 *M* methionine	0.327	0.295	0.146	–	0.086	0.080	0.104	–
0.1 *M* methionine	0.419	0.355	0.305	6.50	0.112	0.095	0.304	6.27
0.2 *M* methionine	0.603	0.525	0.196	–	0.164	0.145	0.173	–
0.05 *M* glutamic acid	0.327	0.295	0.146	–	0.086	0.080	0.104	–
0.1 *M* glutamic acid	0.419	0.355	0.305	6.29	0.112	0.095	0.304	6.27
0.05 *M* urea	0.328	0.328	Nil	–	–	–	–	–
0.1 *M* urea	0.420	0.420	Nil	Nil	–	–	–	–
0.2 *M* urea	0.605	0.595	0.024	–	–	–	–	–
0.3 *M* urea	0.790	0.770	0.038	–	–	–	–	–
0.1 *M* glucose	0.420	0.420	Nil	Nil	–	–	–	–
0.1 *M* sucrose	0.420	0.420	Nil	Nil	–	–	–	–

phosphate bonds. But the results in Table 1 show that in absence of enzymes glucose does not take any part in the combination of adenine or adenosine with H_3PO_4.

In nucleotides containing deoxy-pentose, phosphorylation of the sugar is possible only at C3′ and C5′, since C1′ and C4′ are involved in the furanose ring and C2′ does not bear a hydroxyl group. Adenylic acid, a nucleotide occurring naturally in yeast or in muscle, may be looked upon as adenine-ribose-phosphate or adenosine monophosphate. From the above consideration it is seen that in adenosine monophosphate or adenylic acid, phosphorylation of the sugar can take place at C3′ and C5′.



I



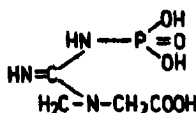
II

Both adenine and adenosine contain the basic NH_2 group while a pentose is linked with adenine to give adenosine. As adenine does not contain a sugar moiety, the equal value of degree of association both in the cases of adenine H_3PO_4 and adenosine H_3PO_4 mixtures obtained in freezing-point as well as boiling-point experiments can only be explained on the basis that H_3PO_4 combines with NH_2 group of both adenine and adenosine to form highly stable complex compounds which are stable even at the boiling-point of the solution. The compounds formed can be depicted by I and II :

The high values of the degree of association 0.596, and the stability constant, 36.51, in freezing-point experiments and 0.571 and 31.02 in boiling-point experiments, when the ratio of adenosine : H_3PO_4 is 1 : 1, show clearly that a remarkably stable phosphorylated compound adenosine monophosphate is formed by the interaction of adenosine with phosphoric acid in complete absence of enzymes. It therefore appears that while in living tissues adenosine di and triphosphates as also adenosine monophosphate are formed under the catalytic action of enzymes only adenosine monophosphate, having the formula shown above, is formed *in vitro* in absence of enzymes.

When creatine is added to H_3PO_4 the freezing-point depression of the mixture is much smaller than the sum of the freezing-point depressions of the constituents. However, glucose added to a mixture of H_3PO_4 and creatine lowers the freezing-point of the resultant mixture to the extent it would do if dissolved in water alone. The degree of association

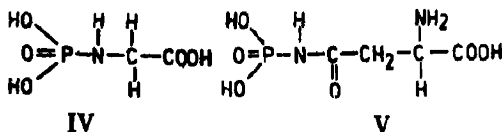
as well as the stability constant value is maximum when the ratio of H_3PO_4 : creatine is 1 : 1 indicating that monomolecular complex phosphocreatine is formed. The boiling-point experiment results show that phosphocreatine is stable even in boiling solution. The formula of phosphocreatine formed *in vitro* is

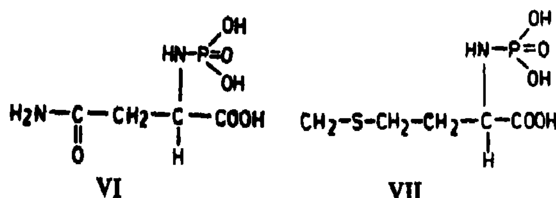


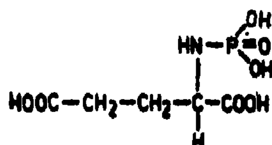
III

The formation of phosphocreatine and its hydrolysis to creatine and phosphoric acid readily occur in muscle aided by an enzyme. But results in Table 1 show that creatine and H_3PO_4 form stable complex in complete absence of enzymes and glucose does not contribute any energy to the formation of this complex although biologists state that in living systems, the energy obtained by the oxidation of glucose or other metabolites under the influence of enzymes are necessary for the formation of phosphocreatine and ATP.

When glycine, asparagine, methionine or glutamic acid is added to H_3PO_4, the freezing-point depression of the mixture in each case is much smaller than the sum of the freezing-point depressions of the constituents. Moreover, the degree of association is maximum when the ratio of H_3PO_4 : amino acid is 1 : 1. The boiling point experiment results are in agreement with the freezing-point data. The results indicate the formation of monomolecular complexes of amino acids with phosphoric acid which are stable even in boiling solution. The complexes may be represented as shown below :







VIII

When urea, glucose and sucrose are added to H_3PO_4, the freezing-point depression of the mixture is equal to the sum of the freezing-point depressions of the constituents when the ratio of the reacting substances is 1 : 1. But in the case of urea, the freezing-point of the mixture is slightly smaller than the additive values when the ratio of urea : H_3PO_4 is 2 : 1 or 3 : 1. These results indicate that although urea contains two NH_2 groups its complex formation tendency with H_3PO_4 is not pronounced and glucose and sucrose do not combine with H_3PO_4 *in vitro* in absence of enzymes.

Results in Table 2 show that when adenine or adenosine is added to H_3PO_4 there is a marked decrease in the specific conductance of the acid. Moreover, the percent decrease in the specific conductance is the same in both the cases when 0.025 *M* adenine or adenosine is added to 0.1 *M* H_3PO_4. If glucose is added to a mixture containing adenine and H_3PO_4 or adenosine and H_3PO_4, a slight decrease in the specific conductance of the mixture is observed. The fall in the specific conductance of H_3PO_4 is maximum when the ratio of adenosine : H_3PO_4 is 1 : 1. These results are in agreement with the freezing-point and boiling-point data.

A marked decrease in the specific conductance of the acid is observed in every case when creatine, glycine, asparagine, methionine or glutamic acid is added to H_3PO_4. The fall in conductivity is maximum when the ratio of creatine or amino acid : H_3PO_4 is 1 : 1. But if excess of creatine or amino acid is added, the corresponding decrease in specific conductance is small showing that monomolecular complexes are formed by the interaction of H_3PO_4 with creatine or amino acid. These results are in agreement with freezing-point and boiling-point data.

When urea is added to H_3PO_4, a fall in specific conductance is observed but the percent decrease is much smaller compared to purines, creatine and amino acid at comparable concentration. This also shows that complex formation tendency of urea is less pronounced.

Table 2 shows that when adenine or adenosine is added to H_3PO_4 there is a marked increase in *p*H of the acid and if 0.025 *M* adenine or adenosine is added to H_3PO_4 the increase in *p*H is the same in both the cases. Moreover, when glucose is added to the mixture containing adenine and H_3PO_4 or adenosine and H_3PO_4 the *p*H of the mixture does not change at all. Similarly when creatine is added to H_3PO_4 a marked increase in *p*H is observed and if glucose is added to the mixture containing creatine and H_3PO_4, the *p*H of the mixture does not change. A marked increase in *p*H is also observed in every case when glycine, asparagine, methionine or glutamic acid is added to H_3PO_4. When the ratio of adenosine or creatine or amino acid : H_3PO_4 is 1 : 1 the change in *p*H is maximum showing that monomolecular complexes are formed by the interaction of purines, creatine or amino acids and H_3PO_4. Thus, *p*H results are also in agreement with freezing-point, boiling-point and conductivity data.

When urea, glucose or sucrose is added to H_3PO_4 the *p*H of the acid does not change showing that urea and carbohydrates do not form complex with H_3PO_4.

TABLE 2

Solutions containing 0.1 M H_3PO_4 and	Specific conductance at 30°	% Decrease	pH	% Decrease in H ion conc.
0.025 M adenine	0.00759	32 35	1.90	49.80
0.025 M adenine+0.05 M glucose	0 00752	32.97	1 90	49.80
0.025 M adenosine	0.00759	32 35	1.90	49.80
0.05 M adenosine	0.00564	49.73	2.15	71.79
0.05 M adenosine+0 05 M glucose	0 00557	50 35	2.15	71.79
0 075 M adenosine	0.00484	56 86	2.45	85 85
0.1 M adenosine	0.00444	60 43	2.70	92.03
0 1 M adenosine+0.1 M glucose	0 00430	61 67	2.70	92.03
0.05 M creatine	0 00692	38.32	1 95	55.38
0 05 M creatine+0.05 M glucose	0 00672	40 10	1.95	55.38
0.1 M creatine	0 00564	49.73	2 25	77.57
0.1 M creatine+0 1 M glucose	0.00537	52 14	2 25	77.57
0.05 M glycine	0.00726	35.29	1.90	49.80
0 1 M glycine	0 00625	44.30	2 15	71.79
0.2 M glycine	0 00591	47 32	2 40	84.14
0 3 M glycine	0.00591	47.32	2 55	88.76
0.05 M asparagine	0 00712	36.54	1.85	43.82
0 1 M asparagine	0 00591	47.32	2 10	68.36
0 2 M asparagine	0 00524	53.29	2 30	80.00
0.05 M methionine	0.00699	37 30	1.85	43.82
0.1 M methionine	0 00578	48 48	2.10	68.36
0.2 M methionine	0 00497	55 70	2 35	82 18
0 05 M glutamic acid	0 00705	31 76	1.85	43.82
0 1 M glutamic acid	0 00578	48 48	2 10	68.36
0 1 M urea	0 01068	4.81	1.60	Nil
0 2 M urea	0 00442	6 95	1 60	Nil
0.3 M urea	0 00108	10 16	1.60	Nil
0.1 M glucose	–	–	1.60	Nil
0 1 M sucrose	–	–	1.60	Nil

An overall examination of the experimental results of freezing point depression, boiling-point elevation, specific conductance and *p*H shows definitely that remarkably stable monomolecular complexes viz. adenine monophosphate, adenosine monophosphate, phosphocreatine and monophosphates of glycine, asparagine, methionine or glutamic acid are formed by the interaction of H_3PO_4 with purines, creatine and amino acids *in vitro* and in complete absence of enzymes These complexes are stable even in boiling solution. Thus a physico-chemical basis of the phenomenon of phosphorylation has been substantiated by cryoscopic, ebullioscopic, conductometric and *p*H determinations.

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Some Thoughts on the Mechanism of Biochemical Reproduction Reactions and Drug Actions

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The mechanism of nature's most baffling process of biochemical reproduction reactions, has been discussed on the consideration of a new type of electrometric-inductive resonance process postulated to operate simultaneously in a group of atleast three structurally related molecules. A quantitative expression in the form of a 'geometrical progression relationship', has been proposed for the growth rate of reproduction of biological species. Various other factors which may influence the kinetics of reproduction reactions have also been discussed.

Proposed mechanism throws considerable light on the drug action of chemotherapic substances, which are structurally related to essential metabolites and thus it can help in the exploration of new drugs for certain unconquered diseases like cancer etc

THE concept of electron transfer processes in biological systems was advanced by Szent-Gyorgyi[1] in 1941. He postulated that the π electrons in excited organic molecules, consisting of conjugated double bonds, might possess the characteristics of "free" electrons analogous to those present in metals and semiconductors; the excited molecules in biological systems rise to common energy levels or continum, along which energy namely, electrons can travel a considerable distance; the motion of electrons is associated with the semiconductors in living systems.

Eley[2,3] and others advanced "Band Model" and "Tunnel Model" for semiconduction properties of organic compounds. Since Szent-Gyorgyi hypothesis, many biochemical problems were considered to be basically the problems of charge or energy transfer over appreciably long distances through rather weakly linked but highly organised systems[4] and various biological processes were attributed to the phenomenon of charge transfer[5-10]. Functional properties of a large number of biological systems were explained through the mechanism of charge transfer along the equal energy level within molecules[7,10].

Brilloni[10,11] proposed that the periodic structure of DNA molecule should give rise to energy bands within the molecules and the donor-acceptor systems should be formed by the energy of bases. Electron transfer from protein to hydrocarbon was attributed as an important step in carcinogenesis[12]. Pullmann[13] gave a quantitative basis for the formation of other charge transfer complexes - the compounds, formed from the interaction of a variety of molecules — primarily aromatics which can behave as electron donor (D), with electron acceptors (A) of various structures.

The basic concept of Szent-Gyorgyi of electron transfer through excited energy level continua and subsequent studies of the behaviour of electron transfer complexes, have provided insight to the mechanism of certain bimolecular interaction processes which occur owing to the presence of charge donor and acceptor groups in the same or two different molecules. Yet these developments have not thrown any light on the most baffling phenomena of nature, namely, bio-chemical reproduction reactions.

In the present paper, the author is proposing a mechanism for these most complicated processes by considering them as 'trimolecular or multimolecular interaction systems of biochemistry'.

The biochemical reactions can be distinguished from the other types of chemical reactions in (a) their "reproduction" behaviour, and (b) in the physiological activity of the substances structurally related to essential metabolites. A biochemical species multiplies itself in its own culture. This reproduction feature is responsible for the growth of entire animal and plant kingdom The mechanism of biochemical reproduction reactions has been explained here on the considerations of a new type of inductive resonance process postulated to operate simultaneously in a group of at least three structurally related molecules. A quantitative expression in the form of a geometrical progression law has been obtained for the growth rate of reproduction of biological species.

The investigations on the biochemical action of several families of synthetic drugs, vitamins and enzymes on substrates have given support to Fildes hypothesis[14] that synthetic substances which are structurally related to essential metabolites destroy the organism by a competitive antagonism of the chemical function of the essential metabolite. However, the mechanism operative in "reproduction reactions", in the competitive growth of virus and bacteria, in the context of a relationship between the structures of enzymes and drugs and their biochemical activities, is not well understood. The metabolic processes which are very specific, differ from other thermodynamic reactions and surface

processes in their low energies of activation and the structural resemblance of the active material with the substrate.

Postulations of the mechanism: The important concepts involved in the theory presented here are as follows:

1. The processes of transfer of electrons to long distances along the chain of atoms in saturated and unsaturated-conjugate bonded systems of organic molecules occur either due to inductometric effect or mesomeric (electrometric) effect or due to the absorption of external energy of a photon.

2. All the above three effects are complimentary and not contradictory to one another and they can occur individually or collectively in biochemical phenomena of nature; further, any one or more of these effects can be responsible for a number of biochemical phenomena and physico-chemical properties of organic systems.

3. The long chains of atoms along which electrons travel, may constitute common energy level continua in molecules and the mobile electrons may behave as free electrons, analogous to those considered to be present in a metal or a semiconductor, and can give rise to semiconduction and other similar properties in organic systems.

4. Accumulation or depletion of these free electrons at certain atoms or groups in a compound may result in the polarisation of the molecules.

5. The molecules under the influence of inductometric effect, electrometric effect and absorption of external energy, may undergo a permanent, periodic or temporary polarisation cum activation respectively and during which period they would be prone to chemical transformation.

6. Since electrons can travel along a chain of atoms in their normal state under electrometric effect, many of the biochemical transformations including reproduction reactions are the consequences of mesomerism, superimposed with inductometric effect of electrophilic and nucleophilic groups of atoms present in organic systems.

7. Reproduction reactions in biochemical systems and drug actions in biological metabolism may involve a trimolecular (or multi-molecular) interaction among structurally related molecules.

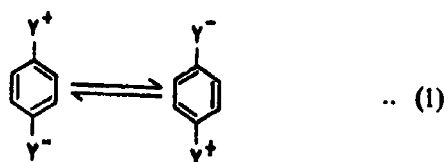
8. When a minimum of three such structurally related molecules come in close vicinity of one another, they form a trimolecular hybrid system designated here as "breathing molecule". This pseudo molecule may undergo mesomeric-inductive-resonance, resulting in the transfer of charges, activation of electrophilic or nucleophilic groups in the two molecules adjacent to the central bridge molecule and finally in the chemical transformation of the adjacent molecules to produce a product identical to the bridge molecule of the pseudo chain of the triplet system.

9. These reproduction reactions may not need any external energy for the excitation of electrons of donor and acceptor groups in the trimolecular hybird system and hence these reactions may occur at the normal energy state of molecules.

The theory: The reactivity of electrometric and nucleophilic groups in organic compounds, which consist of multi conjugated bonds, is largely controlled by the electrometric relay of electric charges from atom to atom down the chain. Such a phenomenon of transmission of electrons within the structures of organic molecules can occur either as a result of elevation of the molecule to a higher energy band through the absorption of external energy of a photon, as conceived by Szent-Gyorgyi[1], or as a result of the transmission of electrons through a molecule in normal state due to mesomerism — the conjugative mechanism of electron displacement. Once a molecule is under mesomeric effect or is excited to higher energy band, the band electrons in either case attains the freedom similar to that of free electrons in metals or semiconductors. These mobile electrons enhance the reactivity of electrometric or nucleophilic groups or say the donor or acceptor capabilities of the groups attached to a molecule. The phenomenon of transmission of electric influence has been discussed in literature with reference to two molecule systems in which one molecule is subjected to the influence of external field of a second polarised molecule through the empty space, instead of through a chain of linkages.

The author postulates that such a phenomenon of mesomerism leading to the electrometric relay of electronic charges through the conjugated bonds and hence to the polarisation of molecules may not be confined to a system consisting of two molecules only wherein the substituent groups of one confers the field effect upon the other. The phenomenon can occur simultaneously in a bunch of a larger number of structurally related molecules as and when they happen to come in close proximity of one another and orient in suitable positions without linking to one another.

Let us consider a molecule of Y—R—Y type which resonates owing to the presence of a pair of conjugate bonds, as schematically indicated in equation 1.

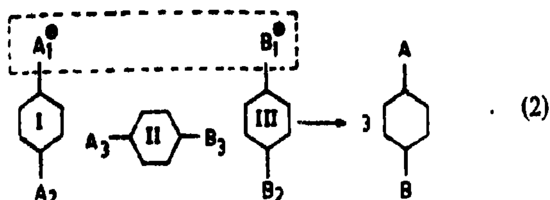


.. (1)

In this process of resonance, a quantum of charge of say δe magnitude rolls in to and fro directions in between carbon atoms 1 and 4 rendering them alternately positive and negative. The resonance brings down the energy of the system and thus keeps Y_1 and Y_2 firmly bound to the benzene nucleus.

Let us consider a reaction system schematically represented in equation 2, where a compound A—R—B of intermediate configuration is present in close proximity and in a suitably oriented position in between the other two molecules

A—R—A and B—R—B of extreme configurations, R being an aromatic or conjugated aliphatic structure and A and B are the substituent electron repellent and electron sink groups respectively. The molecule I possesses only a pair of electron repellent, while the molecule III a pair of electron sink groups. The numbers suffixed to A and B groups represent their respective positions in the hybridised structure.



. (2)

The field effect of groups A_3 and B_3 would impart electrometric influence on the adjacent molecules I and III and disturb their resonance hybrid represented by eq. 1; hence an additional electronic charge of magnitude δe_1 will be drifted in direction of groups A_2 to A_1 in molecule I under the influence of the electron repellent force of the groups A_3 on A_2; while a charge of magnitude say δe_2 would be drifted in the molecule III in the direction B_1 to B_2 owing to the electrophilic nature of the group B_3. The electron charge drift in the two molecules, I and III, would thus be complementary in nature with regard to the direction. Subsequently owing to the symetrical positions of A_1 and A_3 in relation to A_2 and of B_1 and B_3 in relation to B_2, the charge inertia δe_1 and δe_2 will recoil in molecules I and III in the directions A_1 to A_2 and B_2 to B_3 respectively and $(\delta e_1\text{-}\delta e_2)$ in the direction of A_3 to B_3 in the molecule II, bringing the molecules I and III again to their normal states from the activated state.

Thus, under this state, a certain unit of charge relays continuously in to and fro directions in between two "A" groups attached to I and the momentum of the charge inertia is synchronically communicated to the molecule III *via* molecule II. The transmission of the momentum of the charge inertia between the molecules I and III does not impart any strain on the intermediate molecule as the total charge drift through II is only $(\delta e_1\text{-}\delta e_2)$ which is very small in comparison to δe_1 or δe_2. The bridge molecule merely forms a pseudo-chain and thus helps to reduce the activation energy of interactions between I and III, by providing a resonance tunnel through which the electronic charge can roll from one end of the chain to the other.

This hybridised system consisting of three molecules may be designated as a "breathing molecule" and the phenomenon occuring here as "inductive resonance".

In this process of charge relay across the tri-molecular pseudo-chain, the extreme groups A_1 and B_1 are raised to highly activated stage leading to the accumulation of negative charge at group A_1 and simultaneously recedes from electrophilic group B_1 weakening the bond strength between these groups and the benzene nuclei. At this crucial moment of excitation, the molecules I and III are rendered highly placable to chemical transformations such as mutual exchange of the electrophilic groups B_1 and nucleophilic groups A_1, hydrolysis of the molecules, etc. The exchange of A_1 and B_1 groups then result in the formation of three molecules of identical structure A⟨benzene ring⟩B in the presence of a single molecule of the same configuration. This is the phenomenon of "reproduction" which occurs so widely in the animal and plant kingdom. By this mechanism, a molecular species, in presence of structurally related substrates, multiplies itself from 1 to 3 and then to 9 to 27 and so on following the geometrical progression expression 3^n where n represents a particular step in the multiplication process. 'Growth rate factor' of a species can be quantitatively represented by the equation:

$$K=(3X)^{T/t} \quad \dots (3)$$

where $T/t=n$, T being the reaction time (in seconds), t the time (in seconds) taken for the completion of one stage of the growth reaction or say $1/t$ the frequency of multiplication reactions, and X the number of the molecules of the species present at the time $T=0$ which undergoes multiplication. The investigation of Hinshelwood and coworkers[14] on the kinetics of the growth of certain bacteria, supports the above conclusion that the reproduction processes follow a geometrical progression law.

Let us consider an arbitrary example where

$X=1$ molecule of a bacterial species

$t=\frac{1}{4}$ minute

$T=1$ to 60 minutes

Substituting these values in equation 3, we get the values of K which are listed in Table 1.

TABLE 1—REPRODUCTION RATE OF BIOCHEMICAL SPECIES WITHIN 60 MINUTES

Time (T) in minutes	Reproduction number
1	3
2	9
3	27
4	81
5	243
6	729
7	2187
8	6561
9	19683
10	59049
15	1.44×10^{7}
20	3.49×10^{9}
25	8.47×10^{11}
30	2.06×10^{14}
35	5.00×10^{16}
40	1.22×10^{19}
45	2.95×10^{21}
50	7.18×10^{23}
55	1.74×10^{26}
60	4.24×10^{28}

It may be noted from the Table that a species of as large as $\frac{1}{4}$ minute reaction time, grows to 3

numbers in one minute and billions and billions numbers within 60 min. The growth rate can further increase with the decrease of t and further increase with the increase of T. Because of the low values of this factor, t, the virus and bacteria of some of the infectious diseases grow and spread fast. The larger the factor t of a species, the sluggish will be its growth rate.

Special features of the reaction mechanism: It may be noted that these reproduction reactions are initiated only by the product of its reaction. Growth process of these reactions is, therefore, highly specific and a definite species alone can multiply in a particular metabolic environment owing to the dependency of the biological activity upon the chemical constitution of the active materials. The reproduction reactions are irreversible processes as they do not constitute a thermodynamic equilibrium between the reactants and the product.

Factors influencing the kinetics of growth reactions: The kinetics of a reproduction reaction would depend upon the magnitude of the momentum of charge inertia operative in the whole system. If

$$(\delta e_1 \sim \delta e_2) > 0 \quad \ldots (4)$$

the system would be sluggish. On the other hand, if

$$(\delta e_1 \sim \delta e_2) = 0 \text{ or very small} \quad \ldots (5)$$

the trimolecular pseudo-chain would behave as a perfect resonating system wherein the charge pulses would readily be communicated from the molecule I to III and vice versa without straining the molecule II to the least.

The length of R would not impart any steric hindrance to the electrometric relay of charge, provided the conditions of eq. 5 is satisfied. However, the magnitude of T may get altered to some degree with the change in the length of R.

The nature and the positions of the substituent groups would offer the steric hindrance to the relay of the charge and hence would influence the magnitude of charge inertia as expressed by equation 4 A slight change in the nature of the substituent groups or in the structure of the bridging or side arms of the molecules would profoundly influence the degree of activation of the trimolecular pseudo chain systems and the speed of the reaction; a growth reaction may become sluggish or be completely arrested under such a change.

Among the physical factors, light, electrical and magnetic fields and nuclear radiations would influence the speed and the nature of these reproduction reactions to a significant extent.

Bacteriostatic action of drugs: Consider a trimolecular system where the group B_2 in the bridge molecule is replaced by another slightly stronger electron sink (acceptor) group B_2'. The new molecule A_2-R-B_2' by virtue of its stronger groups will replace A-R-B from the breathing molecule and will not allow the formation of fresh trimolecular pseudo-chain system with A-R-B as the bridging molecules. This new trimolecular aggregate would not form a resonance hybrid owing to its asymmetrical structure and thus it would arrest the growth reaction viz., A-R-B multiplication or other types of biochemical processes. Fields' hypothesis of 'metabolic antagonism' as the basis of drug action is explicitly explained by the present theory. The bacteriostatic activity of the sulphonamide and other chemotherapeutic substances[17] is due to their entrance into the reaction ring in competition with the metabolic substrate in an enzyme reaction and thus arresting the later. A chemotherapeutic substance acting as a drug may therefore be defined as "the substance which is structurally related to a metabolic substrate but which differs in one of the substituted groups and is thus capable of upsetting the resonance hybrid and arresting the growth of the virus or bacterial species which is responsible for a disease". Proposed mechanism of reproduction reactions occurring in biological systems, including bacterial and virus, opens new fields for the discovery of many new highly effective drugs for various hitherto unconquered diseases. A deep understanding of the chemistry of human system on the one hand and that of the plants and herbs on the other, in the light of the theory advanced in this paper, can help in the revelation of greater secrets of drug actions.

Explaining the mechanism of nature's most baffling process of biochemical reproduction reactions, the present theory concludes that the biochemical reactions are pure chemical processes independent of life Life in biological organism[18] may be a compendium of multitudes of well organised interlinked chemical processes while the soul imbedded in the life processes is something beyond the materialistic definition and it falls outside the scope of all physical sciences and so this paper.

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4. A prospective contributor should consult recent issues of this journal to get acquainted with its *contents* and *style.* Definitive accounts of significant completed studies presenting new important data or providing a fresh approach to an established subject should be submitted as **articles.** The presentation should be in a logical manner consistent with accuracy, clarity and brevity. The text should be divided into the following sections : (a) Introduction ; (b) Experimental ; (c) Results and Discussion ; (d) References Divisions within the sections should be indicated by sub-headings. **Extensive review and unnecessary details of earlier work should be avoided** Well known or previously published procedures followed in the experimental work should only be referred to, omitting details. Inportant findings and results of much interest which may require priority in publication shall be considered for publication as **notes.**

Any portion of the text for which a special type of print is required must be indicated : **single underlining** for *italic* type and **double underlining** for *bold black* type

The *title* of a contribution should tell accurately and clearly what the paper is about. The first letter of each noun and adjective in the title must be in *capital.* The title shall be followed by the names of the authors and their addresses. The name of the senior author to whom correspondence may be made about the paper must be marked by an asterisk (*) His present address, if different from that quoted as above, must be given in a foot note.

Every article must be accompanied by an informative *abstract* that summarizes the principal findings of the work presented in the paper. Normally it should not be over 3 per cent of the length of the paper and should not exceed 250 words. It should be in a form that it may be used directly for publication in abstracting periodicals. This abstract should be typed before the main text and indented ca. 2 cm to the right of it. *No such abstract is necessary for notes.*

5. The charge carried by an ion should be indicated in the following manner : Na^+, Cu^{2+}, $Co(NH_3)_6^{3+}$, Cl^-, SO_4^{2-}, $Fe(CN)_6^{3-}$, etc. Standard abbreviations should be used throughout the experimental section ; e.g., m.p., b.p., sec, min, hr, mg, g, kg, mm, cm, cps, tlc, uv, ir, nm, etc. Analytical results should be reported in the form : (Found : N, ... ; Cl, ... ; Ni, ... per cent. Calcd. for .. ... ; N ...... ; Cl. ... : Ni. ...... per cent).

6. *Literature citations* **should be numbered consecutively and these numbers are to appear as superscripts in appropriate positions in the text. Care must be exercised for uniformity in reference citations.** "Ibid", "Idem", "et al", etc. should not be used. *Abbreviations for titles of journals must ordinarily conform to those used by the "Chemical Abstracts" published by the American Chemical Society (vide : "List of Periodicals Abstracted"). References to uncommon journals should also give the corresponding Chemical Abstract references.* **All the references must be typed in their serial order at the end of the text in the manuscript. The names (not surnames only) of all the authors shall be given.** A few sample citations are noted below :

1. P. C. RAY, *J. Indian Chem. Soc.*, 1924, **1**, 207.
2. R. J. KULA, D. T. SAWYER, S. I. CHAN and C. M. FINLEY, *J. Amer. Chem. Soc.*, 1963, **85**, 2930.
3. C. S. GARNER and D. A. HOUSE in "Transition Metal Chemistry", (Ed.) R. L. CARLIN, Marcel Dekker, New York, 1970, Vol. 6, p. 59.

Foot notes must be referred to in the text with suitable symbols such as *, †, ‡, §, ‖, etc.

7. **Instructions for Diagrams and Figures :** The number of tables, diagrams and photographs should not be more than what is absolutely necessary, in view of the fact that the reproduction of such materials is very costly. **If these exceed 20% of the pages of the text, authors may be asked to pay for the excess cost.**

a. Figures should be numbered with Roman numerals and mentioned consecutively in the text indicating their respective locations. *All Figures must have legends and these should be typed out separately in a sheet of paper at the end of the main text of the manuscript.* **Legends should not duplicate information in the text.**

b. One set of the drawings should be made with India ink on tracing cloth or good quality white drawing paper. *Graph paper must not be used.* Lines should contrast sharply with the back-ground. **Most drawings should be planned for reproduction to a column width of 7.5 cm. Lettering should be large enough to be 1.5 mm high after reduction.** Large drawings should be simplified for submitting with the manuscript, in a size which is reducible to not more than 16 cm × 22 cm. For satisfactory reproduction all drawings should be approximately twice the size in which they are to appear in the print. Use of legends in the body of the diagrams must be reduced to the minimum. Free hand drawings and drawings unsuitable for block making cannot be accepted. If necessary the Editors may get the figures redrawn properly for which the actual cost is to be borne by the author(s). Structures and formulae which cannot be composed must also be submitted as suitable drawings for blockmaking.

c. If original tracings are not available, glossy prints of the tracings can be used if the back-ground is clear and the lines are distinct.

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8. *Reprints* shall be supplied only on receipt of payment of the due charges, i.e., 50 reprints @ Rs. 15/- (U. S. $ 5.00 for foreign) per page or part thereof, subject to a minimum charge of Rs. 35/- (U. S. $ 12.50 for foreign) 100 reprints of 1-2 pages @ Rs. 50/- and for subsequent 2 pages or part thereof @ Rs. 40/-, next 100 reprints or part thereof at half the original rate. For foreign, 100 reprints @ U. S. $ 8.00 per page or part thereof subject to a minimum U. S. $ 20.00. Next 100 reprints or part thereof at half the original rate. *Additional postage is to be paid for Air Mail Charge. No free reprints are supplied and no such request can be entertained.* Reprint order form is sent to author with the proof.

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10. **In case of rejection of a paper, the opinion of the Honorary Editor shall ordinarily be treated as final.**

J. Indian Chem. Soc.,
Vol. LIX, May 1982, pp. 609-616

Syntheses of Some Terpenoids via Nickel Tetracarbonyl Induced Cyclisation*

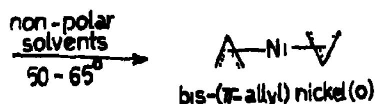
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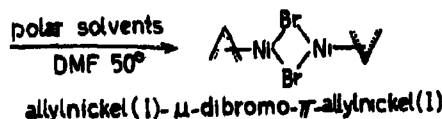
Department of Chemistry, Panjab University, Chandigarh-160 014

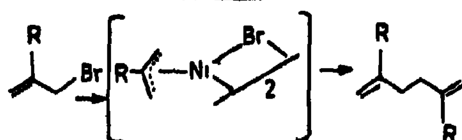
ON this occasion I convey my sincere thanks to the Indian Chemical Society for giving me this opportunity to deliver the Acharya J. C. Ghosh Memorial Lecture. Acharya Ghosh's contribution to the cause of science and education in India stands out as a lighthouse for the younger generation of scientists and will continue to inspire them in their pursuit for better understanding of the world of science.

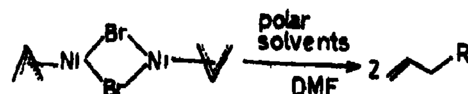
Few subjects have perhaps made greater progress within the last decade than organic synthesis involving organo-metallics reagents. Partly because of this reason I have chosen for to-day's talk an aspect of organo-metallic chemistry which involves π-allyl nickel intermediates and their applications in the field of terpenoids.

Carbon-Carbon bond formation via π-allyl nickel complex









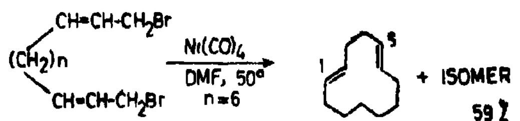
Scheme 1

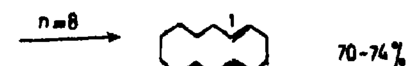
The π-nickel complexes shown in Scheme 1 are formed in good yields by the reaction of a variety of allyl bromides with an excess of $Ni(CO)_4$ in dry benzene at 50° under inert atmosphere[1]. These complexes are relatively inert towards alkyl halides *in hydrocarbon or ether type solvents*[2]. In polar, co-ordinating media, viz., DMF, N-methyl pyrrolidine, hexamethyl phosphoramide etc., a facile reaction occurs between the complex and a wide variety of organic halides including vinyl and aryl halides to furnish coupled products in high yields.

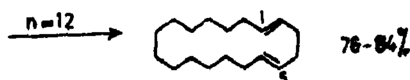
It may be pointed out here that the treatment of π-complexes with dissimilar allyl halides can result in an exchange reaction giving rise to a new π-nickel allyl complex with the resultant formation of a mixture of coupled products. If the allyl group in the allyl halide and π-nickel complex is the same, the reaction is then normal.

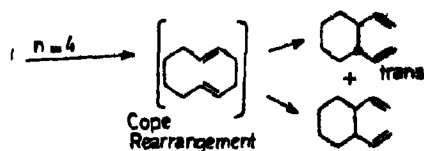
Intramolecular coupling :

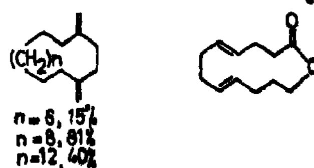
An intramolecular version of this reaction has been usefully extended to the synthesis of cyclic 1,5-diene systems using appropriate *bis*-allylic halides and employing high dilution technique to inhibit the intermolecular reaction[3]. The cyclic 1,5-diene moieties have invariably *trans-trans* geometry irrespective of the stereochemistry of the olefinic linkages in the starting *bis*-allylic halides. Application of this technique has been made in achieving the syntheses of naturally occurring 12, 14 and 18 membered ring compounds including *humulene, casbene, cembrene and macrolides in* yields ranging from 60-80%.











Scheme 2

* Acharya J. C. Ghosh Memorial Lecture (1979) delivered under the auspices of Indian Chemical Society on 27th December 1981 at Madras.

As shown in Scheme 2, when the value of $n=2$ or 4 in the acyclic *bis*-allylic halides, the formation of 6-membered ring is favoured relative to 8 or 10 membered rings. The cyclic intermediate, 1, 5-diene, formed is believed to undergo Cope's rearrangement resulting in the formation of substituted 6-membered rings.

In the first case the formation of 4-vinyl cyclohexene took place preferentially to 8-membered ring and where $n=4$, the product consisted entirely of a mixture of *cis*- and *trans*-1, 2-divinyl cyclohexene. This selective course of the reaction has been exploited in designing a synthetic route to naturally occurring monocyclic sesquiterpene, elemenes.

Another gratifying aspect of this coupling reaction is the compatibility of the presence of an array of additional functional groups in the starting allylic halides, such as isolated double bonds, keto or ester groups, which we have also amply demonstrated in some of the syntheses of the naturally occurring terpenoids, I am going to discuss.

Synthesis of (±) *cubitene, a 12-membered monocyclic diterpene :*

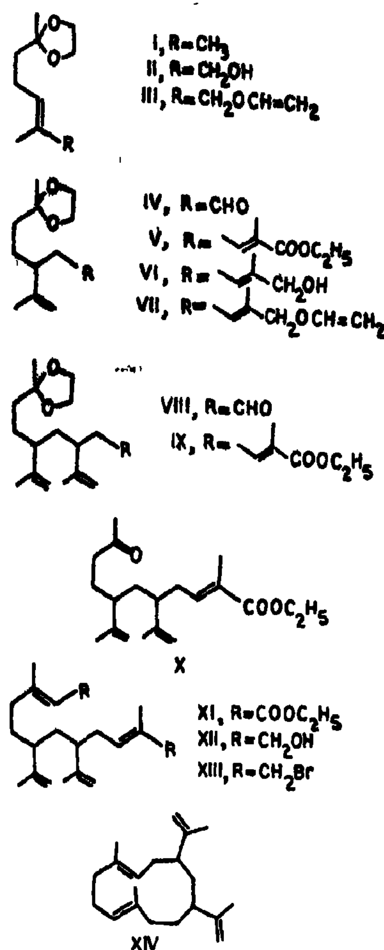
A novel irregular 12-membered monocyclic diterpene hydrocarbon, cubitene, was recently isolated as a major constituent of the defensive secretions released from the frontal glands of soldiers of East-African termite *Cubitermes umratus* Williams[8]. On the basis of spectral studies, chemical reactions and X-ray diffraction data, it was shown to be (8S, 10R)-1, 5-dimethyl-8, 10,-*bis*(isopropenyl)cyclododeca-1(E), 5(E)-diene.

The salient features of the structure are the presence of a 12-membered monocyclic ring with two isopropenyl substituents and two triply substituted olefinic bonds in the form of 1, 5-diene unit in the macrocyclic ring.

The two E-trisubstituted double bonds which are part of the 1,5-diene moiety of cubitene have been created by nickelcarbonyl coupling reaction. This coupling reaction has been found to give mixtures of double bond isomers regardless of the homogeneity of the precursors when triply substituted double bonds are involved. Therefore, the stereochemistry of these two double bonds in cubitene precursors was not an important consideration.

The reaction sequence employed for the synthesis is shown in Scheme 3.

The starting material for the synthesis was the easily available methylheptenone ketal (I) which was subjected to selenium dioxide oxidation to the allylic alcohol (II) which was converted into the corresponding vinyl ether (III) through mercuric acetate catalysed transetherification with ethylvinyl ether. Claisen rearrangement of this vinyl ether under nitrogen atmosphere furnished the ketal aldehyde (IV) with one isopropenyl substituent at



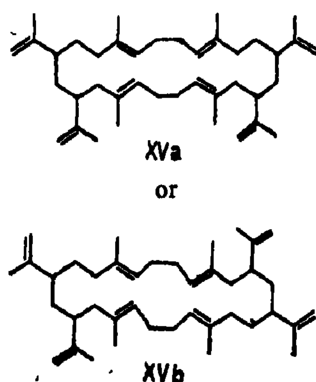
Scheme 3

the C-3 position. Modified Wittig reaction of ethyl α-diethyl phosphonopropionate in diglyme on this ketal aldehyde gave ethyl 8-ethylenedioxy-5-isopropenyl-2-methyl non-2-enoate (V) which was found to be predominantly an E-isomer as indicated by its pmr analysis (E : Z : : 4 : 1).

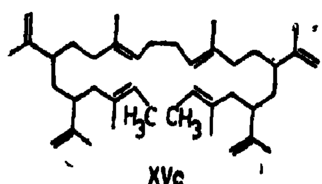
No attempt was, however, made to separate the two isomers because both the isomers were expected to lead to the same aldehyde after reduction, vinyl etherification and Claisen rearrangement.

On LAH reduction in dry benzene at 60° this conjugated ester gave the carbinol (VI) which on usual equilibration with excess of ethyl vinyl ether provided 8,8-ethylenedioxy-5-isopropenyl-2-methyl-1-vinyloxy-non-2-ene (VII), which after purification was submitted to Claisen rearrangement under nitrogen atmosphere at 190-95° for 30 min when it generated the olefinic aldehyde (VIII) as a pleasant smelling liquid. This was subjected to modified Wittig reaction with ethyl α-diethyl-phosphonopropionate to afford the conjugated ester (IX). Confirmation of the E stereochemistry of conjugated ester was obtained from its pmr spectrum which showed C_3 proton at δ 6.7.

The compound was deketalised with PTS in acetone-water at room temperature to give ethyl 5,7-*bis*(isopropenyl)-2-methyl-10-oxo-2(E)-undecenoate (X). Modified Wittig reaction on this keto-ester with ethyl-diethylphosphonoacetate under the usual reaction conditions yielded a stereoisomeric mixture of (E, E) and (E, Z)-diesters (XI) (6 : 1), diethyl 2,6-dimethyl-5,7-*bis*(isopropenyl) dodeca-2,10-dien-1,12-dioate in which the (E, E) isomer was predominant as indicated by pmr spectrum. No attempt was made to separate the isomers. As has been stated earlier, whatever be the nature of olefinic linkages in the starting allylic halides, the composition of the isomers in the cyclised product remains the same. Reduction of this diester with LAH in dry benzene gave the diol (XII) as a viscous liquid which was converted into the corresponding dibromide (XIII). The labile allylic dibromide was reacted with nickel tetracarbonyl in DMF at 47-50° under nitrogen atmosphere. The cyclisation product showed two distinct spots (R_f 0.93, 0.76) on tlc analysis, using *n*-hexane as the solvent system, indicating the presence of two components. The two components were separated by column chromatography over $AgNO_3$ impregnated silica gel. The less polar major component (R_f 0.93) was obtained in 10% yield and its identity was established by comparison of its spectral data with those reported for natural cubitene. The second product (R_f 0.76 ; 3% yield) appeared to be a dimer of cubitene as revealed by its pmr spectrum which had very close resemblance with that of cubitene, except the allylic methyl signals which in the case of the dimer appeared at δ 1.62. The high resolution mass spectrum of this dimer showed a molecular ion (M^+) at m/e 544.5 corresponding to the molecular formula $C_{40}H_{64}$ of the dimer. Thus the dimer could be assigned the cyclic structure shown below.



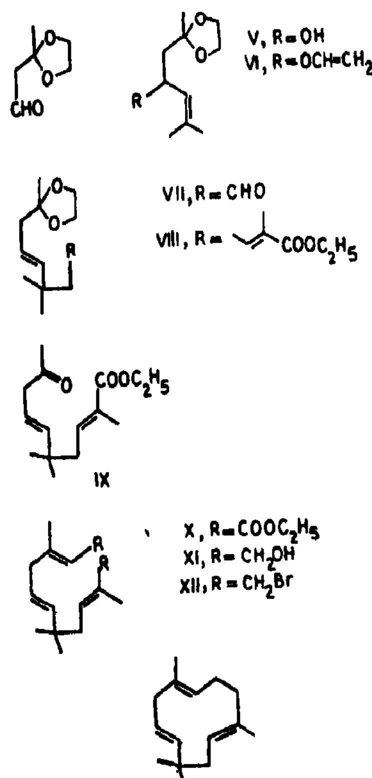
This structure of the dimer was supported by its ir and nmr data also.



The possibility of acyclic dimer XVc was ruled out on the basis of pmr and mass spectral analysis. For acyclic components vinyl methyl H 30 and M^+ at m/e 546.5.

A new synthesis of humulene :

Humulene, a monocyclic sesquiterpenic hydrocarbon has been isolated from the oil of hops, *Humulus lupulus* Linn. and the essential oil of wild ginger, *Zinziber zerumbut*[6]. As a result of the comprehensive chemical, spectroscopic and X-ray crystallographic studies, it has been assigned the structure 2,6,6,9-tetramethylcycloundeca-1,4,8-triene. Structural features of the humulene molecule are presence of 11-membered ring with a gem dimethyl substituent, two *trans* triply substituted double bonds in the form of 1,5-diene unit in the macrocyclic ring and a doubly substituted *trans* double bond between C_4 and C_5 in the ring. The above structure was further corroborated by a synthesis by Corey and Hamanka[4]. We have accomplished a facile synthesis of this hydrocarbon which is based on the application of $Ni(CO)_4$ catalysed cyclisation for the creation of a cyclic 1E,5E-diene moiety, and for the fixation of *trans* geometry of C_4 bond Claisen rearrangement of the properly substituted allyl vinyl ether has been used. Sequence of reaction is shown in Scheme 4.



Scheme 4

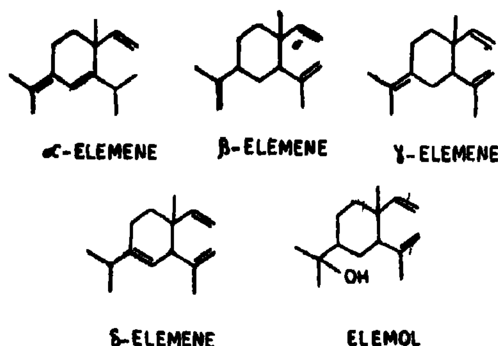
3,3-Ethylenedioxybutanal (IV) was subjected to Grignard reaction with isobutylenmagnesium-bromide in dry THF to afford the carbinol (V) in 76% yield. Equilibration of this alcohol with excess of ethylvinyl ether in the presence of catalytic

amount of freshly crystallised mercuric acetate provided 6,6-ethylenedioxy-2-methylhepten-2-yl vinyl ether which after chromatographic purification was subjected to pyrolysis under nitrogen atmosphere at 190-95° to get the sharp smelling aldehyde, 3,3-dimethyl-7,7-ethylenedioxy-*trans*-4-octen-1-al (VII) in 94% yield. The *trans* nature of the disubstituted double bond in the aldehyde (VII) was established by its ir absorption which showed prominent peak at 975 cm^{-1}. This aldehyde was submitted to modified Wittig reaction with ethyl α-diethylphosphonopropionate to have ethyl 9,9-ethylenedioxy-2,5,5-trimethyl-*trans*-2-*trans*-6-decadien-1-oate (VIII) as the major, higher boiling product which was deketalised with 10% HCl in acetone to yield the keto ester (IX) in 84% yield. Modified Wittig reaction with ethyl diethylphosphonoacetate in diglyme on the keto ester furnished predominantly the all *trans*-diester. However, no attempt was made to separate the all *trans*-diester from the *cis-trans* isomer because both of them would yield the product as a mixture of isomers regardless of the homogeneity of the precursors.

The conjugated diester was reduced with LAH at room temp to the corresponding diol which after conversion into the dibromide with PBr_3, was cyclised with $Ni(CO)_4$ in DMF to furnish humulene. The crude product was purified by column chromatography over $AgNO_3$ impregnated silica gel, followed by distillation under reduced pressure. The synthetic product was found to be identical (ir, pmr) with a natural sample kindly supplied by Dr. Sukh Dev.

Syntheses of elemene group of sesquiterpenes :

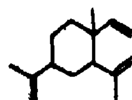
Some members of the elemene group of sesquiterpenes are shown below :



The salient structural features of this class are the presence of a vinylic group together with an angular methyl on the same carbonyl atom of the trisubstituted cyclohexane skeleton and two other olefinic bonds which are not in conjugation except in α-elemene.

The main difficulty in devising a clean synthesis of a particular hydrocarbon of this class is the fixation of these sensitive olefinic bonds in the desired position unambiguously and introduction of the angular methyl group.

Synthesis of β-elemene :



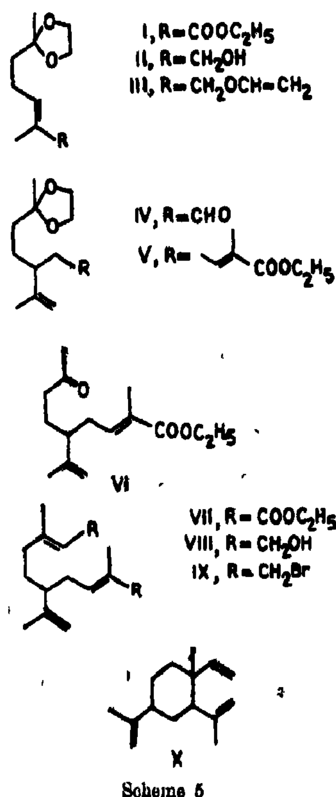
β-ELEMENE

β-Elemene is a constituent of many essential oils, e.g. Sweetflags, Juniper, Orange and Elecampane[7]. On the basis of comprehensive chemical and spectroscopic studies the structure shown above has been assigned to β-elemene. The projected synthesis of β-elemene has been designed on the findings of Corey *et al* that the formation of a 6-membered ring relative to 8 and 10-membered ring is favoured when an acyclic terminal *bis*-allylic dihalide of the type



$$Br.CH_2.CH{=}CH.(CH_2)_nCH{=}CH.CH_2Br$$
$$(n = 2, 4)$$

is cyclised with nickel carbonyl in a suitable solvent. Appropriately substituted allylic acyclic dibromide required for the synthesis of β-elemene was procured through the sequence of reactions as depicted in Scheme 5.



Scheme 5

The starting material, ethyl 2-methyl-6,6-ethylenedioxy-*trans*-2-heptenoate (I) was prepared as reported in literature. This, on reduction with LAH, afforded 2-methyl-6,6-ethylenedioxy-*trans*-2-hepten-1-ol (II) in quantitative yields. Equilibration of this allylic alcohol with excess ethylvinyl ether

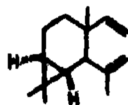
in presence of catalytic amount of freshly crystallised mercuric acetate provided the vinyl ether (III) in 80% yield. The Claisen rearrangement of the purified material under nitrogen atmosphere in a sealed tube at 190-195° generated as high as 82% yield of the corresponding aldehyde (IV) which was characterised through its semicarbazone derivative. The aldehyde so obtained was submitted to modified Wittig reaction with ethyl α-diethylphosphonopropionate in presence of NaH when 2-methyl-5-isopropenyl-8,8-ethylenedioxy *trans*-2-nonenoate (V) was obtained in excellent yield.

This compound on deketalisation with dilute hydrochloric acid and acetone afforded ethyl 2-methyl-5-isopropenyl-8-oxo-*trans*-2-nonenoate (VI). This keto-ester on being submitted to modified Wittig reaction with ethyl diethylphosphonoacetate under the usual conditions furnished a mixture of ethyl 2,8-dimethyl-5-isopropenyl-undeca-*trans*-2-*trans*-8-diene-1,10-dioate and ethyl 2,8-dimethyl-5-isopropenyl-undeca-*trans*-2-*cis*-8-diene-1,10-dioate isomers in which the *trans*-2-*trans*-8 isomer (VII) was predominant. However, no attempt was made to separate the two isomers as both are expected to give the same final compound, β-elemene. The diester thus obtained was reduced with LAH to have the diol (VIII) as a viscous liquid which was converted into the corresponding dibromide (IX) with PBr_3 in ether. The allylic dibromide on cyclisation with nickel carbonyl according to the conditions of Corey *et al* was transformed into β-elemene (X).

The synthetic hydrocarbon, after chromatography through florosil column, showed a single spot on tlc supporting the fact that both the *trans* and *cis* allylic dibromides on cyclisation with nickel carbonyl yield the same product. The identity of the synthesised product with the natural β-elemene was established by comparison of ir and pmr spectra.

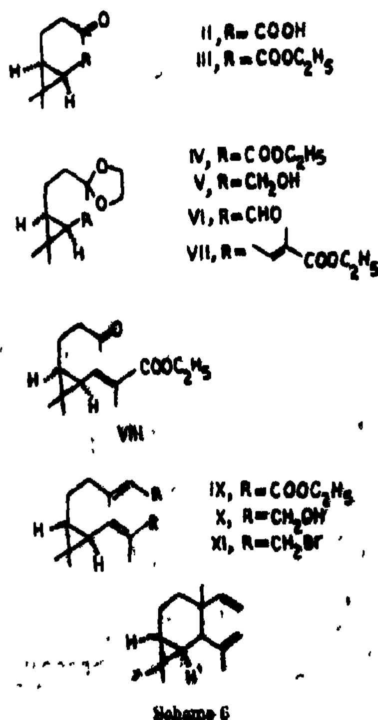
Synthesis of dl-bicyclo elemene :

A bicyclic sesquiterpene hydrocarbon, (–)-bicycloelemene, was isolated from peppermint oil of Bulgarian origin by Herout *et al*[8] and also from cold pressed peel oil of Yoza by Shinoda *et al*[9]. The following structure was assigned to it on the basis of comprehensive chemical and spectral studies :



Using the nickel carbonyl induced cyclisation of the appropriate *bis*-allyl dibromide, a racemate of bicycloelemene has been synthesised.

The starting material *cis*-(dl)-1,1-dimethyl-2-(3'-oxobutyl) cyclopropane-3-carboxylic acid (I) was procured through condensation of methyl heptenone with ethyl diazoacetate in the presence of $CuSO_4$. It was esterified and then ketalised to



Scheme 6

give the ketal ester (III) in 80% yield. Reduction with LAH in dry ether furnishes the corresponding carbinol (V) which on oxidation with Collin's reagent gave the ketal aldehyde (VI). Modified Wittig reaction of ethyl α-diethylphosphonopropionate on the ketal aldehyde gave a stereoisomeric mixture of the esters in which the *trans* isomers predominated. The higher boiling *trans*-ketal ester on deketalisation with PTS in acetone provided the keto-ester which on submission to modified Wittig reaction with ethyl diethylphosphonoacetate furnished the diester as a stereoisomeric mixture containing mainly the *trans, trans* isomer. However, no attempt was made to separate the all *trans*-isomer because the stereochemistry of the double bonds in the starting *bis*-allylic halides does not affect the composition of the isomers in the cyclised product in the $Ni(CO)_4$ induced coupling reaction.

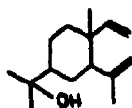
This diester upon LAH reduction produced the diol as a viscous liquid which was transformed into the corresponding dibromide and subsequently subjected to nickel carbonyl induced cyclisation according to the conditions of Corey to furnish (dl)-bicycloelemene.

The chromatographed (silica gel) synthetic product was characterised through the comparison of its ir, pmr with that of the authentic sample kindly supplied by Dr. K. Nishimura. GLC analysis of the synthesised product also showed it to be a pure material.

Synthesis of β-elemene and elemol :

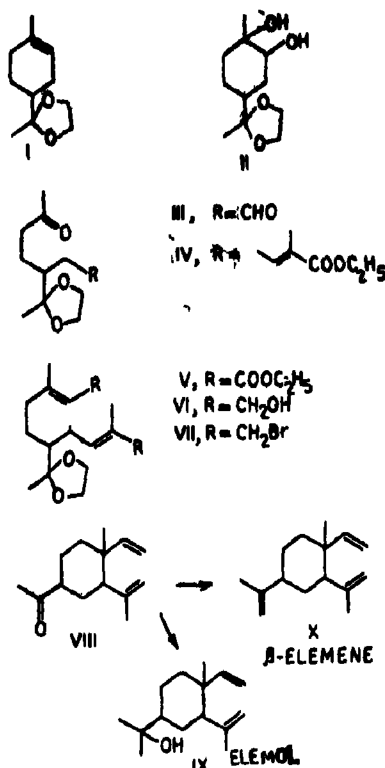
Elemol is a constituent of Manila elemi oil[10] and Java citronella oil. On the basis of chemical

reactions and spectral data elemol has been assigned the structure shown below :



ELEMOL

This structure has been confirmed by Corey *et al* through a synthesis. Making use of the $Ni(CO)_4$ cyclisation reaction we have also accomplished synthesis of elemol and β-elemene from the common intermediate. Scheme of reactions is shown in Scheme 7.



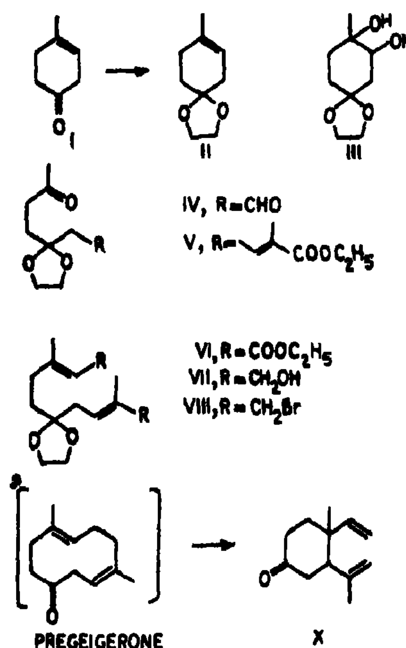
Scheme 7

The starting compound, 1-, methyl-4(1',1'-ethylenedioxyethyl)cyclohexane-1, 2-diol (II) was prepared by the alkaline $KMnO_4$ oxidation of 1-methyl-4(1',1'-ethylenedioxyethyl)-1-cyclohexane (I) in 30% yield. This diol upon oxidation with lead tetraacetate in dry benzene provided the keto aldehyde (III) which was subjected to selected Wittig reaction with α-ethoxy carbonylethylidene-triphenylphosphorane in refluxing benzene to yield 8-carbethoxy-5(1', 1'-ethylenedioxyethyl) non-*trans*-7-ene-2-one (IV) in 70% yield. In view of the fact that the reaction of the phosphonate carbanion with aldehydes yields only *trans* isomer, this compound was given the *trans* olefin configuration. This keto ester was submitted to modified Wittig reaction with ethyl diethylphosphoneacetate using diglyme as solvent and sodium hydride as a base to furnish the diester (V) as a mixture of (E,E) and (E,Z) isomers. However, no attempt was made to separate the all *trans*-isomer from the *trans, cis*-isomer, because of the observed non-stereospecificity of nickel carbonyl cyclisation reaction on the nature of the double bonds in the starting allylic halides. The unsaturated diester (V) was smoothly reduced with LAH in dry ether at low temp to the diol (VI). The diol was converted into corresponding dibromide (VII) with PBr_3 in the presence of a little pyridine. The compound got deketalised during the formation of dibromide. This was indicated by the ir adsorption peak at 1710 cm^{-1}. As the presence of carbonyl group in the *bis*-allyl bromide does not interfere with the reaction of organo-nickel complexes, this keto dibromide was subjected as such to the nickel carbonyl induced cyclisation. Three spots in tlc analysis (pet. ether · ether : : 4 : 1) indicated the presence of three components in the cyclised product. The most polar *trans* component (R_f 0.03) was separated through column chromatography (AgNO$_3$ impregnated silica gel) and was subjected to the well known Wittig reaction with methylene triphenylphosphorane to furnish β-elemene. The identity of the hydrocarbon was established through comparison of its ir and nmr spectra.

The intermediate, *trans*-ketone was subjected to Grignard reaction with methylmagnesium iodide to afford the *tert*-carbinol, elemol, whose identity was also established through its ir and pmr spectra.

Synthesis of (±)—geijerone :

Geijerone has been isolated from the essential oil of *Juniperus communis* Linn. by Thomas. On the basis of chemical as well as spectral evidence its constitution was established as 3-isopropenyl-4-methyl-4-vinylcyclohexanone. We have been able to synthesise this ketone through the use of nickel-carbonyl induced cyclisation.



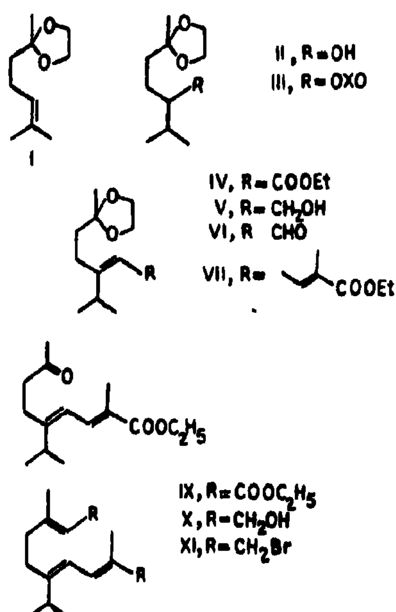
Scheme 8

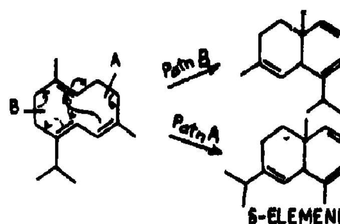
The starting material, 4, 4-ethylenedioxy-1-methyl-1-cyclohexene (II), was prepared in 85% yield by ketalisation of 4-methylcyclohexen-3-one (I). This was subjected to alkaline $KMnO_4$ oxidation to yield the diol (III), which on oxidation with lead tetraacetate in dry benzene gave the aldehyde (IV). Selective Wittig reaction of α-ethoxycarbonyl ethylidenetriphenyl phosphorane on the keto aldehyde in refluxing dry benzene yielded 5,5'-(ethylenedioxy)-8-carbethoxy-8-methyl-7(E)-nonen-2-one (V) in 70% yield. This *trans*-keto ester was submitted to Horner Wittig reaction with ethyl diethylphosphoneacetate in diglyme to furnish the diester (VI) which was smoothly reduced to diol (VII) with LAH, converted into dibromide (VIII) with PBr_3/ether and finally cyclised with nickel tetracarbonyl according to Corey's conditions to get geijerone (X). It is formed through Cope rearrangement of the intermediate pregeigerone, formed during the nickel carbonyl cyclisation. The synthetic hydrocarbon was purified by chromatography over silica gel column, eluting with pet. ether (40-60°) containing 10% ether. It was characterised through comparison of its ir and nmr spectra with that of an authentic sample.

Synthesis of δ-elemene :

δ-Elemene, a monocyclic sesquiterpene hydrocarbon, was isolated by Hildebrand and Sutherland from the wood oil of *Dysoxylon frazeranum* which is a commercial timber in Que nsland[11]. Lateron, the same hydrocarbon was isolated from a gurjum balsam from Chittagong (Bangladesh) by Sutherland *et al.* The structure was assigned to this hydrocarbon on the basis of detailed study of its chemical behaviour and spectral data.

Using the nickel tetracarbonyl induced cyclisation we have tried to effect a synthesis of δ-elemene with the reaction sequence shown in Scheme 9.





Scheme 9

2, Methyl, 6, 6-ethylenedioxy-2-heptene (I) on hydroboration/oxidation reaction provided 6, 6-ethylenedioxy-2-methyl-hept-3-ol (II) in 75% yield. This alcohol was smoothly oxidised with Collins reagent to give the corresponding ketal ketone (III) which was subsequently submitted to modified Wittig reaction with ethyl diethylphosphonoacetate and sodium hydride in diglyme as solvent to afford ethyl 6, 6-ethylenedioxy-3-isopropyl-hept-2-enoate (IV). Reduction of this ketal ester with LAH gave 6, 6-ethylenedioxy-3-isopropylhept-2-enol (V) which was again oxidised with Collin's reagent to afford the aldehyde (VI) in 80% yield. The ketal aldehyde thus obtained was further submitted to modified Wittig reaction with ethyl α-diethylphosphonopropionate and the resulting ketal-ester (VII) was deketalised with dil HCl in acetone to have ethyl 8-oxo-2-methyl-5-isopropyl-non-2, 4-dienoate (VIII) in 85% yield. This keto-ester was again submitted to modified Wittig reaction with ethyl diethylphosphonoacetate to get the diester (IX) which was as usual reduced to diol (X), converted into allylic dibromide (XI) and cyclised through reaction with $Ni(CO)_4$ in DMF. An interesting observation was made when we proceeded to isolate the final expected δ-elemene. In the pmr spectrum of the synthetic sample, there appeared two sharp signals instead of one as expected, at 8.3 and 8.4 δ, suggesting thereby that there were two types of allylic methyl groups present. This prompted us to think that our synthetic sample could be a mixture of δ-elemene and a small amount of its isomeric compound. The formation of these could be visualised because, theoretically, the 10-membered cyclic intermediate is a 1, 5-diene which could cleave in two possible ways through Cope's rearrangement (cf. Scheme 9) and hence could yield a mixture of two products.

The glc analysis showed the synthetic sample to be a mixture of two compounds, almost in equal proportions. However, the work is still in progress whereby we wish to separate the two components and establish their individual identity.

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Physico-Chemical Studies of Some Mixed Ligand Complexes of Samarium(III) and Holomium(III)

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Stability constants of mixed ligand complexes of Sm(III) and Ho(III) with cyclohexanediaminetetraacetic acid (CyDTA) as primary ligand and Alizarin Reds (ARS), 8-hydroxyquinoline-5-sulphonic acid (OSA) or iminodiacetic acid (IMDA) as secondary ligand were determined potentiometrically at 0.05, 0.10, 0.15, 0.20 and 0.25 ionic strengths in aqueous medium at 30°. Ionic strength data are utilized to establish the applicability of Bronsted equation at lower ionic strengths. The thermodynamic stability constants, log K_1^H, log K_2^H and log K_{MAL}^{CyDTA} at zero ionic strength are also determined. The influence of solvent media is studied by evaluating stability constants in 25, 40, 50, 60 and 75% dioxan-water mixtures at 30° and 0.1 M ionic strength in addition to the study in aqueous medium as mentioned earlier.

THE present communication describes the stability constants of ternary complexes of Sm(III) and Ho(III) with cyclohexanediaminetetraacetic acid (CyDTA) as primary ligand and Alizarin Red S (ARS), 8-hydroxyquinoline-5-sulphonic acid (OSA) and iminodiacetic acid (IMDA) as secondary ligands in aqueous medium at ionic strengths 0.05, 0.1, 0.15, 0.20 and 0.25 *M* at 30° and in different compositions of dioxan-water media, 25, 40, 50, 60 and 75% at 0.1 *M* ionic strength.

Some work have been reported[1,2] on the influence of ionic strength and dielectric constant of the medium on the stability constant of binary systems. The present study deals with a systematic study of stability constants of some ternary systems (i) in aqueous medium of various ionic strengths and (ii) in dioxan-water mixtures of different compositions. The former study helps in understanding the effect of number of electrolyte ions and the latter gives information about the influence of dielectric constant on the stability of complexes.

The formation constants of mixed-ligand chelates using CyDTA as primary ligand have been determined using Irving-Rossotti *p*H titration technique[3]. Recent findings indicate that the rare earth ions[4,5] are considered to expand their coordination number to larger than six. The assumption of coordination number of eight for Sm(III) and Ho(III) seems to explain the experimental observations more satisfactorily than a coordination number of six in cases of ternary systems, as reported in this paper. The choice of the secondary ligands was done on the basis of different bonding groups present so as to see the effect of different ionic strength and different dielectric constant of media on the protonation constants and stability constants of the ternary systems using them.

Experimental

Materials : All chemicals used were of reagent grade purity. The ligand solutions were prepared by dissolving ARS (E. Merck), OSA (E. Merck) and IMDA (B D.H.) in double distilled water. A stock solution of disodium salt of CyDTA (Koch-light) was prepared by dissolving the calculated amount of the acid in the required volume of standardized NaOH solution. Metal solutions were prepared from their chlorides (Indian Rare Earth Ltd.) by dissolving in known quantity of perchloric acid and were estimated complexometrically[6].

Apparatus : An expanded scale *p*H-meter (ECIL) with accuracy ±0.02 *p*H units was employed to measure *p*H or 'B' values (*p*H-meter reading). All experiments were carried out in an atmosphere of nitrogen. The temperature was maintained constant with a ultracryostat bath (MK 70, Germany) having an accuracy of ±0.02°.

Procedure For the study of ternary complexes following four mixtures were prepared :

a. $2.0\times10^{-3}M$ perchloric acid,

b. $2.0\times10^{-3}M$ perchloric acid + $1.0\times10^{-3}M$ secondary ligand,

c. $2.0\times10^{-3}M$ perchloric acid + $1.0\times10^{-3}M$ CyDTA solution + $1.0\times10^{-3}M$ metal solution, and

d. $2.0\times10^{-3}M$ perchloric acid + $1.0\times10^{-3}M$ CyDTA solution + $1.0\times10^{-3}M$ metal solution + $1.0\times10^{-3}M$ secondary ligand.

In each case total volume was made upto 100 ml by adding required amount of double distilled water or purified dioxan as the case may be. The ionic strength was maintained by adding appropriate amount of neutral sodium perchlorate solution. In all the cases the ratio between metal, CyDTA and secondary ligand was kept 1 : 1 : 1. These mixtures were titrated with standardized NaOH. A modified form of Irving-Rossotti titration technique was used for the calculation of log K_{MAL}^{CyDTA}. In case of water-dioxan solvent media,

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS AND MIXED-LIGAND STABILITY CONSTANTS IN MEDIUM OF DIFFERENT IONIC STRENGTHS AT 30°

System	Constants	Ionic strength					
		0	0.05	0.10	0.15	0.20	0.25
H-ARS	log K_1^H	11.18	11.06	11.00	10.92	10.82	10.75
	log K_2^H	5.43	5.37	5.33	5 28	5 24	5.21
H-OSA	log K_1^H	8 63	8.52	8 45	8.38	8.30	8.26
	log K_2^H	3 92	3.85	3.78	3.72	3.68	3 65
H-IMDA	log K_1^H	9.52	9.46	9.35	9 27	9.18	9 12
	log K_2^H	2 80	2.74	2 70	2.65	2.62	2 58
[Sm(III)(CyDTA)(ARS)]	log K	6.58	6.44	6 36	6.30	6.25	6 21
[Sm(III)(CyDTA)(OSA)]	log K	3 85	3 75	3.68	3 60	3 54	3 50
[Sm(III)(CyDTA)(IMDA)]	log K	3 40	3 35	3 28	3 20	3 12	3 08
[Ho(III)(CyDTA)(ARS)]	log K	6 86	6.76	6 70	6.63	6.58	6 55
[Ho(III)(CyDTA)(OSA)]	log K	4.36	4 23	4 15	4 08	4 02	3 98
[Ho(III)(CyDTA)(IMDA)]	log K	3.89	3.82	3.75	3.62	3.55	3.50

TABLE 2—PROTON-LIGAND AND MIXED LIGAND STABILITY CONSTANTS IN DIFFERENT COMPOSITIONS OF DIOXAN-WATER MIXTURES AT FIXED IONIC STRENGTH μ=0.1M AND T=30°

System	Constants	Dioxane%					
		0	25	40	50	60	75
H-ARS	log K_1^H	11 00	11 05	11 12	11.21	11 35	11 55
	log K_2^H	5 33	5 38	5 54	5 70	5 92	6 28
H-OSA	log K_1^H	8 45	8 58	8 83	9.06	9 42	9 95
	log K_2^H	3 78	3 82	3 95	4 08	4 27	4 46
H-IMDA	log K_1^H	9 35	9 47	9 62	9 73	9 86	10.12
	log K_2^H	2 70	2 75	2 90	3 04	3 16	3.32
[Sm(III)(CyDTA)(ARS)]	log K	6.36	6.47	6 62	6 75	6.92	7 18
[Sm(III)(CyDTA)(OSA)]	log K	3 68	3 85	4 03	4 16	4 40	4.65
[Sm(III)(CyDTA)(IMDA)]	log K	3 28	3 41	3.55	3 68	3 80	4 06
[Ho(III)(CyDTA)(ARS)]	log K	6 70	6 88	6 95	7 06	7 22	7.53
[Ho(III)(CyDTA)(OSA)]	log K	4 15	4.30	4.45	4 68	4 78	5 08
[Ho(III)(CyDTA)(IMDA)]	log K	3 75	3 86	3 98	4 07	4 24	4.52

the 'B' values were used for the calculation of pL, instead of pH values, where 'B' denotes the pH-meter reading only and not the actual pH, as the pH-meter was calibrated with aqueous buffers. The use of pH meter reading 'B' instead of true pH values did not make any difference[6,7] in the calculation of free ligand concentration and was usually valid for water-dioxan media

Results and Discussion

The values of proton-ligand stability and mixed ligand stability constants at different ionic strengths and at 30° are given in Table 1. The thermodynamic stability constants pK_1^o, pK_2^o and log K_1^o, calculated using Bronsted equation at zero ionic strength, are also recorded in this table. Stability constants of various mixed ligand complexes studied and the proton-ligand stability constants of the secondary ligands in mixed solvents of different dielectric constants are summarised in Table 2.

Method of interpolation at various $\bar{n}A$ or $\bar{n}$ values was employed for the computation of proton-ligand and mixed ligand stability constants.

The plot of log K_{MAL}^{CyDTA} against $\sqrt{\mu}$ and plot of log K_{MAL}^{CyDTA} vs mole fraction of dioxan for [Ho(III)(CyDTA)(L)] systems are represented in Fig. 1 and Fig. 2, respectively. Similar plots for the Sm(III) mixed ligand complexes and the proton-ligand systems were obtained.

Influence of ionic strength on proton-ligand and mixed ligand systems : It may be seen from the data in Table 1 that increase in ionic strength decreases the values of log K_1^H, log K_2^H and log K_{MAL}^{CyDTA}. These data were analyzed by Bronsted equation

$$\log K = \log K^{\circ} + A\Delta Z^{2} \sqrt{\mu} \quad \ldots (1)$$

where A is the Debye-Hückel constant, ΔZ^2 is the difference in square of the charge of product and reacting ions and K° is the formation constant at zero ionic strength. The plots of log K_1^H, log K_2^H or log K_{MAL}^{CyDTA} against $\sqrt{\mu}$ show almost linear relationship for the entire range of ionic strength.

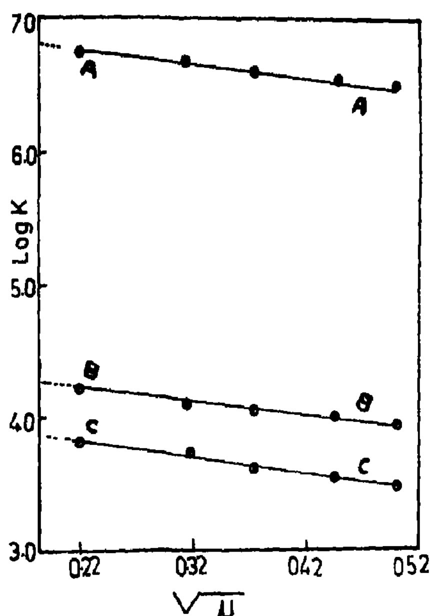


Fig 1 A plot of log K against √μ
A A [Ho(III)CyDTA(ARS)]
B B [Ho(III)CyDTA(OSA)]
C C [Ho(III)CyDTA(IMDA)]

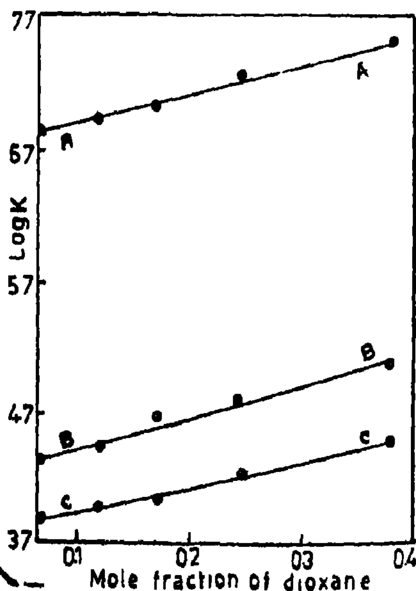


Fig. 2 A plot of log K against mole fraction of dioxan
A.A. [Ho(III)(CyDTA)(ARS)]
B B [Ho(III)(CyDTA)(OSA)]
C.C. [Ho(III)(CyDTA)(IMDA)]

This proves the validity of the Bronsted equation at low ionic strengths.

Influence of dielectric constant : It is seen from Table 2 that log K_1^H, log K_2^H and log K_{MAL}^{CyDTA} values increase with percentage increase of dioxan in the mixture, as is well known. The stability constants of mixed ligand complexes are considerably influenced by the dielectric constant of the solvent medium because both primary complex and the secondary ligands are charged. Similarly, there is increase in proton-ligand stability because protons are held by a solvent with a predominant basic property.

It is worthwhile to mention that the experimental evidences of formation of mixed ligand complexes in the present study are also in favour of expansion of coordination number of Sm(III) and Ho(III) in case of mixed ligand complexes with CyDTA acting as primary ligand. The relative order of stability in terms of metal ions is Ho(III) > Sm(III) which can be explained on the basis of decreasing size and increasing charge/radius ratio of the metal ions.

Acknowledgement

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Characterisation of Some Solid Products Obtained by Carrying Out the Replacement Reactions on the Hydrated Sulphates of Copper(II), Nickel(II) and Cobalt(II) Using Two Different Heterocyclic Ligands viz., Antifuran-2-carboxaldoxime and 2-pyrrolidone

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Treatment of hydrated sulphates of copper(II), nickel(II) or cobalt(II) with the two ligands, antifuran-2-carboxaldoxime (FDH) and 2-pyrrolidone (pyrr) separately, forms compounds: $[Cu(FDH)(H_2O)_2]SO_4$, $[Ni$ or $Co(FDH)(H_2O)_4]SO_4$, $[Cu(pyrr)(H_2O)_2]SO_4$ and $[Ni$ or $Co(pyrr)(H_2O)_4]SO_4$. The analytical, molar conductance, magnetic and spectroscopic data suggest square planar structure for copper(II) complexes and octahedral structure for nickel(II) and cobalt(II) complexes.

IT was shown in our earlier publications that a number of solid complexes were obtained by replacing some of the coordinated water molecules from Cu(II), Ni(II) and Co(II) hydrated sulphates by using such neutral ligands as aromatic and heterocyclic amines, thiourea, heterocyclic Schiffs bases and oximes[1-3]. In most of the cases only two water molecules could be replaced easily while the third one could be replaced only if some stronger ligands like chelating di or triamines were used[1-3]. The present paper deals with a similar study using antifuran-2-carboxaldoxime and 2-pyrrolidone as ligands.

Experimental

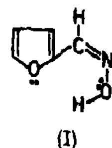
A known weight of hydrated copper(II), nickel(II) or cobalt(II) sulphate was suspended in methanol and equimolar amount of the ligand, dissolved in methanol, was added dropwise while the mixture was kept under reflux continuously*. After the addition of the ligand was completed, the reaction mixture was further refluxed for 5 hr and the complex was crystallized out from the solution by repeated treatment with petroleum spirit.

Discussion

On the basis of elemental analysis and molar conductanee values (Table 1), the molecular formulae assigned to the complexes are $[Cu(FDH)$ or $(pyrr)(H_2O)_2]SO_4$ and $[Ni$ or $Co(FDH)$ or $(pyrr)(H_2O)_4]SO_4$ which show that only two coordinated water molecules have been replaced from the parent hydrated metal(II) sulphate by one ligand molecule. In the ir spectra of all these complexes a sharp νOH band characteristic of coordinated water appears at ~3420 cm^{-1} while the bands due to ν_3 and ν_4 modes of uncoordinated sulphate ions appear at 1110 and 650 cm^{-1}, respectively.

The thermogravimetric measurements on the complexes in the temperature range of 20 to 800° show no weight loss around 100° indicating the absence of lattice water. The loss in weight between 240 and 400° corresponds to the loss of two molecules of water and one molecule of the ligand. The metal(II) sulphate, thus formed remains stable between 400 and 500° and decomposes to the metal oxide upto 600° which remains stable till 800°.

In the spectrum of the free ligand antifuran-2-carboxaldoxime (I), the bands corresponding to the



(I)

intramolecularly bonded –OH group appear at 3160 and 3040 cm^{-1}, while these merge together in the complexes and only one sharp band appears at 3360 cm^{-1}. This shows the cleavage of hydrogen bonding of oxime oxygen[6-7], which is also supported by the raising of $\nu C=N$ of the free ligand from 1640 to 1660 cm^{-1} in the complexes[8,9]. Furthermore, the appearance of two sharp bands at 670 ($\nu M-O_{oxime}$) and 510 cm^{-1} ($\nu M-O_{furan}$) suggests the coordination of the ligand through furan ring and oxime oxygens[10-12].

* Even if the ligands are added in excess only one equivalent of the same (corresponding to the replacement of two water molecules) is consumed in the reaction. The other equivalents remain unreacted even after continued refluxing.

TABLE 1—ANALYTICAL, MAGNETIC, MOLAR CONDUCTANCE AND TGA DATA OF COMPLEXES

Complexes	%M	%C	%H	%N	$\%SO_4$	% of H_2O and ligand lost at 280-400°	μ_{eff} in B M.	λ in mhos in nitro benzene
1. $[Cu(FDH)(H_2O)_2]SO_4$	20.95 (20.72)*	20 15 (19 57)	3 60 (2 95)	4.70 (4 56)	31 99 (31 31)	48 09 (47 96)	1 884	24.8
2. $]Ni(FDH)(H_2O)_4]SO_4$	14.98 (15 70)	15.87 (16.06)	3 10 (3 50)	3.27 (3 74)	24 81 (24 69)	53 98 (54 20)	3 208	26 2
3. $[Co(FDH)(H_2O)_4]SO_4$	16 71 (17.42)	16 97 (17 76)	3 43 (3 87)	4 02 (4 14)	27 48 (28 41)	54 10 (54 18)	4 950	25 0
4 $[Cu(H_2O)_2(pyrr)]SO_4$	22 10 (22 67)	16 92 (17.11)	3 56 (3 92)	4 81 (4 92)	33 62 (34 22)	42 99 (43 13)	1 882	22 6
5. $[Ni(H_2O)_4(pyrr)]SO_4$	17 41 (18.82)	14 93 (15 40)	5 05 (4 84)	4 30 (4 49)	29 44 (30 79)	50 80 (50 36)	3 082	21 9
6. $[Co(H_2O)_4(pyrr)]SO_4$	17.20 (18 87)	16 01 (15.39)	4 94 (4 84)	4 50 (4 40)	29 81 (30 77)	50 07 (50 34)	4.608	28 2

* The figures in parenthesis indicate Calcd values

In free 2-pyrrolidone, the >NH and >C=O stretching frequencies are observed at 3300 and 1700 cm^{-1}, both of which undergo considerable negative shift in complexes and occur at 3250 cm^{-1} and 1665 cm^{-1} respectively showing coordination through these sites.

The copper(II) complexes are, thus, four coordinate with μ_{eff} values in the range 1 82-1.88 B.M. The appearance of a band at ~1600 cm^{-1} associated with a shoulder at ~1300 cm^{-1} is indicative of a square planar stereochemistry.

The μ_{eff} values of both the nickel(II) complexes are around 3.20 B.M. suggesting an octahedral stereochemistry. In the electronic spectra, three bands at 25,310, 13,980 and 9,660 cm^{-1}, assigned to $3A_{2g} \rightarrow 3T_{1g}(P)$ (ν_3), $3A_{2g} \rightarrow 3T_{1g}(F)$ (ν_2) and $3A_{2g}(F) \rightarrow 3T_{2g}(F)$ (ν_1) transitions, along with the D_q and B values of 966 cm^{-1} and 850 cm^{-1} confirm an octahedral structure[13-16].

The room temperature μ_{eff} values of the two cobalt(II) complexes may either indicate a tetrahedral or octahedral structure but the values at two lower temperatures (257°K, 143°K) show a considerable decrease as shown below, suggesting the latter geometry since the μ_{eff} values for the tetrahedral complexes should be independent of temperature[17].

	μ_{eff} at 303°K	μ_{eff} at 257°K	μ_{eff} at 143°K
Complex no. 3	4.95 B.M.	4.36 B.M.	3.92 B.M.
Complex no. 6	4.61 B.M.	4.08 B.M.	3.65 B.M.

This assignment of octahedral structure is further confirmed by the presence of a sharp band at 20,000 cm^{-1} $[4T_{1g}(F) \rightarrow 4T_{1g}(P)]$ and another weak and broad one at 9,900 cm^{-1} $[4T_{1g}(F) \rightarrow 4T_{2g}(F)]$ and the derived D_q and B values of 844 and 879 cm^{-1} [18-21].

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Nitrato-Complexes of Y(III), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) with 2-(2′-Pyridyl)Benzimidazole

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The nitrato-complexes, $[Y(PyBzH)_2(NO_3)_2]NO_3.H_2O$ and $[Ln(PyBzH)_2NO_3.OH.H_2O]NO_3.nH_2O.mC_2H_5OH$ [Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho; n=1-3, m=0-0.5; PyBzH=2-(2′-pyridyl)benzimidazole] are formed on interaction of the ligand with metal nitrates in ethanol. The electrical conductance values (116-129 $ohm^{-1}cm^2mol^{-1}$) suggest 1 : 1 electrolyte-nature of the complexes. Magnetic moment values of Ce(2 53 B.M), Pr(3.62 B.M.), Nd(3.52 B.M), Sm(1 70 B M.), Gd(8.06 B M.), Tb(9.44 B.M.), Dy(10 56 B M.) and Ho(10.51 B.M.) in the complexes confirm the terpositive state of the metals. Infrared evidences are obtained for the existence of both coordinated (C_{2v}) and uncoordinated (D_{3h}) nitrate groups Electronic absorption spectra of Pr(III)-, Nd(III)-, Sm(III)-, Tb(III)-, Dy(III)- and Ho(III)-complexes have been analysed in the light of LSJ terms.

THE N-heterocycles, for example, 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy), usually being less basic than most of the amines, are more useful as nitrogen-donors for the lanthanides. The 1,10-phenanthroline complexes of the type $Ln(phen)_2(NO_3)_3$ were reported by Hart *et al*[1] and 2,2′-bipyridyl complexes of the type $Ln(bipy)_2(H_2O)_n(NO_3)_3$ by Sinha[2] The study of these complexes leads one to conclude that aromaticity enhances the chelating ability of the heterocyclic ligands.

The ligand, 2-(2′-pyridyl)benzimidazole (PyBzH) having the same coordination site, $-N=C-C=N-$, as phen or bipy has been shown in our previous communication[3] to form isothiocyanato-complexes of the lanthanides by partial replacement in $Ln(NCS)_6^{3-}$. Here we report the nitrato-complexes of PyBzH with Y(III), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III).

Experimental

Preparation of the ligand · 2-(2′-Pyridyl)benzimidazole was prepared by the condensation of *o*-phenylenediamine with picolinic acid by the method cited in literature[4].

Metal nitrates: The hydrated crystals of metal(III) nitrates, obtained from Indian Rare Earths, Kerala, in 99.9-99.99% purity were used as such.

Preparation of the complexes: A mixture of the ethanolic solution of metal nitrate and the ligand in 1 : 2 molar proportion was refluxed for a few min when a solid started separating; the heavier the metal, the quicker was the separation. The mixture was refluxed for about 1 hr to ensure complete digestion. The solid was filtered, washed thoroughly with hot ethanol and dried over $CaCl_2$

Physical measurements: Electrical conductances were measured with Philips PR 9500 Resistance Bridge using dip-type cell, calibrated with KCl solution. Magnetic susceptibility measurements were made on a Gouy magnetic balance calibrated[5] with $Hg[Co(NCS)_4]$, diamagnetic corrections being made using Pascal's constants[6]. Infrared spectra were scanned on Beckman IR-12 in KBr discs through commercial services of the Regional Sophisticated Instrumentation Centre, IIT, Madras Electronic spectra were recorded on Cary 14 and Cary 17 spectrophotometers using matched silica cells.

Results and Discussion

Stoichiometry Y(III)-nitrate, on interaction with 2-(2′-pyridyl)benzimidazole in ethanol, forms the 8-coordinate dinitrato-*bis*(ligand)yttrium(III) nitrate monohydrate, $[Y(PyBzH)_2(NO_3)_2]NO_3.H_2O$. The nitrates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III), however, form the 8-coordinate hydroxo-aquonitrato-complexes of the general formula, $[Ln(PyBzH)_2NO_3.OH.H_2O]NO_3.nH_2O.mC_2H_5OH$. Water and/or alcohol of crystallisation is lost by heating upto 120° in each of these complexes and the coordinated water by heating upto 200°. The 1 : 1 electrolyte nature of the compounds is supported by their electrical conductance values of 116-129 $ohm^{-1}cm^2mol^{-1}$ in DMF at 304°K (Table 1).

Magnetic moments: The room-temperature magnetic moment values (Table 1) of Ce(III) (ground state term: $^2F_{5/2}$), Pr(III)($^3H_4$), Nd(III)-

* For correspondence.

TABLE 1—CHARACTERISATION DATA

Complex		%M	%N	%C	%H	% loss in wt 120°	% loss in wt 200°	Molar cond. ($ohm^{-1}cm^{2}$) 304°K	μ_{eff} (B.M.)
$[Y(PyBzH)_2(NO_3)_2]NO_3.H_2O$	R*	13.01	18.11	42.18	2.95	2.63	-	117	—
	F	13.37	18.86	42.50	2.70	2.59			
$[La(PyBzH)_2NO_3\,OH.H_2O]NO_3\,1.5H_2O$	R	19.41	15.65	40.29	3.38	3.77	2.51	116	—
	F	19.63	15.83	40.70	3.01	3.81	2.33		
$[Ce(PyBzH)_2NO_3.OH\,H_2O]NO_3\,3H_2O$	R	18.81	15.07	38.76	3.66	7.21	2.12	118	2.53(297°)
	F	18.55	15.16	39.00	3.50	7.01	2.13		
$[Pr(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,1.5H_2O$	R	19.64	15.62	40.18	3.37	**	**	119	3.62(297°)
	F	19.03	15.77	40.10	3.30				
$[Nd(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,1.5H_2O$	R	20.01	15.55	39.99	3.96	3.71	2.19	128	3.52(297°)
	F	19.76	15.85	40.00	3.40	3.81	2.37		
$[Sm(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,2.5H_2O$ $0.5C_2H_5OH$	R	19.58	14.59	39.10	3.80	**	**	129	1.70(297°)
	F	19.58	14.36	39.20	4.00				
$[Gd(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,H_2O$	R	21.68	15.47			2.19	2.19	124	8.06(306°)
	F	21.56	15.61			2.51	2.52		
$[Tb(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,2H_2O$	R	21.30	15.05			4.80	2.67	120	9.14(306°)
	F	20.82	15.02			4.20	2.67		
$[Dy(PyBzH)_2NO_3.OH\,H_2O]NO_3\,0.5C_2H_5OH$	R	22.13	15.26	40.87	3.27	3.13	2.45	118	10.56(306°)
	F	21.90	15.17	41.03	4.11	3.54	2.15		
$[Ho(PyBzH)_2NO_3\,OH\,H_2O]NO_3\,H_2O$	R	22.53	15.30			2.16	2.16	116	10.51(306°)
	F	22.38	15.52			2.28	2.57		

PyBzH = $C_{12}H_9N_3$ *R = required, F = found **Could not be done on account of low yield

($^4I_{9/2}$), Gd(III)($^8S_{7/2}$), Tb(III)($^7F_6$), Dy(III) ($^6H_{15/2}$) and Ho(III)($^5I_8$) agree well with the formula[7]: $\mu_{eff}=g[J(J+1)]^{\frac{1}{2}}$. The magnetic moment of Sm(III) ($^6H_{5/2}$; 1.70 B.M.) is higher than the calculated value of 0.84 B.M. because of the appreciable population in some excited J-levels lying much closer to the ground level[7].

Infrared spectra · The NH stretching frequency of PyBzH appearing in the region 3150-3030 cm^{-1} suggests that the imidazole NH remains undeprotonated[8-10]. Broad absorption bands in the region 3525-3200 cm^{-1} are ascribed to ν(OH) indicating the presence of water (coordinated, uncoordinated or hydrogen-bonded) or alcohol[11]. Bending mode of H–O–H appears in the range 1640-1615 cm^{-1} in each compound and that of M–O–H near 1160-1150 cm^{-1} in all the complexes except that of Y(III).

A coordinated nitrate (C_{2v}) is expected to exhibit six fundamentals[12]. The highest frequency band, $\nu_4(B_1)$, appears as a very strong broad multiplet in the range 1530-1435 cm^{-1}, obscuring the weak ligand bands at 1485 and 1460 cm^{-1}. The $\nu_1(A_1)$ mode appears in the range 1350-1298 cm^{-1} as a strong band in every complex. On the basis of the magnitude of $\nu_4-\nu_1$ (La: 190, Ce: 200, Pr. 190, Nd: 230, Sm. 190, Y: 175, Gd: 182, Tb · 182, Dy: 175, Ho: 172 cm^{-1})[13] and other arguments placed in one of our previous communications[14], we assume that the nitrate is bidentate.

The weak bands at 1040 and 798 cm^{-1} of PyBzH are highly intensified in the complexes, slightly shifted in position and sometimes accompanied by shoulders or satellites. These are assigned to $\nu_2(A_1)$ and $\nu_6(B_2)$ vibrational modes, respectively, though the latter may very well be treated as ν_4(E') of the ionic nitrate, discussed later. The strong absorption band at 749 cm^{-1} of the organic ligand is shifted slightly to the higher frequency side in the complexes (La. 75?, Ce. 745, Pr 755, Nd: 752, Sm · 755, Y: 755, Gd · 748, Tb 745, Dy: 745, Ho: 750 cm^{-1}) and shoulders appear in Y-, La-, Ce-, Pr- and Tb- complexes in the range 760-745 cm^{-1}, which may be assigned to $\nu_3(A_1)$ vibrational mode of the C_{2v}-nitrate. However, in Nd- and Sm- complexes, the main 752 cm^{-1} band extends with possible multiplets upto 760 cm^{-1} making it broader. A weak to medium intensity band at 715-700 cm^{-1} in each of La, Ce-, Pr-, Nd-, Gd-, Tb-, Dy- and Ho- complexes correspond to $\nu_5(B_1)$ mode of $C_{2v}-NO_3$.

At least two of the three infrared active fundamentals, expected for uncoordinated nitrate (D_{3h}), are observed The ν_3(E') mode appears as shoulder in the range 1400-1372 cm^{-1}. There is an extremely weak absorption in the ligand at 813 cm^{-1}, but in every complex there is a strong band near 820-813 cm^{-1}, which is ascribed to $\nu_2(A''_2)$ mode of the D_{3h}-nitrate It has already been mentioned that 798-795 cm^{-1} band may be treated as $\nu_6(C_{2v}-NO_3)$ or $\nu_4(D_{3h}-NO_3)$.

Electronic spectra · The electronic spectra of the complexes have been recorded in DMF. The sulphur-yellow Ce(III)-complex shows a strong absorption near 450 nm on account of *4f→5d* transition[15].

The $^1G_4$(9.80 kK), $^3F_4$(6.85 kK), $^3F_3$(6.41 kK), $^3F_2$(4.69, 4.95, 5.08 kK) and $^3H_6$(4.46 kK) levels of Pr(III)[16], not located earlier in the aquo-ion[17,18] or in the terpyridyl system[18], have been located apart from the $^3P_2$(22.47 kK), $^3P_1$(21.28 kK), $^3P_0$(20.70 kK) and $^1D_2$(16.81 kK) levels. The

extent of red-shifts suggests a meagre nephelauxetic effect.

The band positions of Nd(III), $^4F_{3/2}$ (11.30, 11.51 kK), $^4F_{5/2}$ and $^2H_{9/2}$ (12.16, 12.50 kK), $^4S_{3/2}$ (13.46 kK), $^4F_{7/2}$ (13.60 kK), $^4F_{9/2}$ (14.81 kK), $^2H_{11/2}$ (15.92 kK), $^2G_{7/2}$ (17.18 kK), $^4G_{5/2}$ (17.48 kK), $^4G_{7/2}$ (19.05 kK), $^4G_{9/2}$ (19.47 kK), $^2D_{3/2}$ (21.05 kK), $^4G_{11/2}$ (21.60 kK), $^2P_{1/2}$ (23.31 kK) assigned on the basis of calculated[19,20] and aquo-ion values[17,18,21] indicate that PyBzH produces even smaller nephelauxetic effect than bipy does[22].

The Sm(III) J-levels, $^6H_{15/2}$ (6.15-6.63 kK), $^6F_{5/2}$ (7.14 kK), $^6F_{7/2}$ (7.98 kK), $^6F_{9/2}$ (9.17 kK), $^6F_{11/2}$ (10.53 kK) and ^6P (24.75 kK) have been located as in $LaCl_3$-host[23].

The J-levels of Gd(III), all expected in the ultraviolet region[24], could not be located on account of strong ligand absorptions in that region.

The bands $^7F_2$ (4.94, 5.03 kK), $^7F_1$ (5.35 kK), $^5D_3$ (26.18 kK) and $^5L_{10}$ (27.17 kK) of Tb(III) suffer little red-shift with reference to the positions in $LaCl_3$-host[25]. Again, there are practically no red-shifts in Dy(III) bands[26], $^6H_{9/2}$ and $^6F_{11/2}$ (7.66, 7.72 kK; hypersensitive), $^6H_{7/2}$ and $^6F_{9/2}$ (9.01 kK), $^6H_{5/2}$ (10.20 kK), $^6F_{7/2}$ (10.93 kK), $^6F_{5/2}$ (12.36 kK) and $^6F_{3/2}$ (13.16 kK) and so also in Ho(III) bands[27], $^5I_7$ (4.93 kK), $^5I_6$ (8.42, 8.51, 8.68 kK), $^5I_5$ (11.30 kK), $^5F_5$ (15.50 kK), $^5S_2$ (18.12 kK), $^5F_4$ (18.59 kK), $^5F_3$ (20.66 kK), $^5F_2$ (21.05 kK), $^3K_8$ (21.37 kK), $^5G_6$ or $^5F_1$ (22.12 kK) and $^5G_5$ (23.70 kK).

The spectral data thus suggest that the extent of covalency decreases with increasing *f*-orbital occupancy.

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Cu(I), Ag(I), Tl(I), Zn(II), Cd(II) and Hg(II) Complexes of 1-Amino-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol

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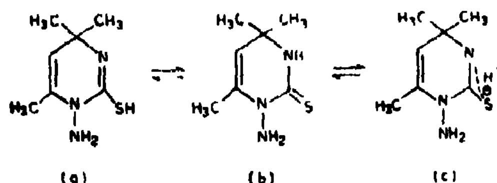
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Complexes of Cu(I), Ag(I), Tl(I), Zn(II), Cd(II) and Hg(II) with 1-amino-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol have been isolated and characterized by elemental analysis, ir and magnetic measurements. The complexes of copper, silver and thallium are polymeric in nature. Their probable structures are proposed.

1-SUBSTITUTED-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiols are versatile analytical reagents[1-4]. However, no attempt has so far been made to isolate and study the structures of solid complexes of these ligands. The isolation of Cu(I), Ag(I), Tl(I), Zn(II), Cd(II) and Hg(II) complexes with 1-amino derivative of the thiol and their structural features are reported in the present communication.

Experimental

Preparation of the ligand and its metal complexes. The ligand (I) was prepared by the method of Mathes[5]. It is highly soluble in DMSO but sparingly so in alcohol. It is almost insoluble in water.



1-Amino-4,4,6-trimethyl-1H,4H-pyrimidine-2-thiol (I)

Ammonia (50%) was added to aqueous solutions of nitrates of Ag(I) and Tl(I) and sulphates of Cu(II), Cd(II) and Zn(II) till there was a distinct smell of ammonia. NH_4Cl (2-3 g) was also added in case of Zn to avoid its hydrolysis. The clear solutions thus obtained were boiled and mixed with the hot solution of the ligand (in 1 : 1 DMSO-alcohol mixture). The metal-ligand ratio was kept slightly more than 1 : 1 in case of Ag and Tl and 1 : 2 in other cases.

The Cu(I), Ag(I) and Tl(I) complexes precipitated immediately and settled down as amorphous mass on digesting over a water bath for 1 hr. Zn(II) and Cd(II) complexes separated slowly as colourless crystals. The compounds were filtered, washed with hot water, hot DMSO-water mixture (1 : 9), ethanol and ether, and dried *in vacuo* over P_4O_{10}. Yield 75-80%.

About 1.4 g of $HgCl_2$ was dissolved in 100 ml ethanol and filtered. The filtrate was mixed with the ligand solution in hot 1 : 1 DMSO-ethanol mixture and heated on a water bath for 1 hr. The yellowish white complex was filtered, washed with hot water, 10% DMSO and ethanol, and dried at 110°.

Magnetic measurements were made by Gouy's method at 300°K. IR spectra in the range 4000-650 cm^{-1} were recorded on a Perkin-Elmer 137 Infracord spectrophotometer in KBr medium, and in the range 600-200 cm^{-1} on a Perkin-Elmer 621 grating recording spectrophotometer in nujol mull.

The metal content of the complexes was estimated by the standard methods[6] and sulphur as $BaSO_4$. C, H and N were estimated microanalytically.

Results and Discussion

Elemental analyses (Table 1) of the complexes reveal that metal to ligand ratio is 1 : 1 in Ag(I), Cu(I), Tl(I) and Hg(II) complexes and 1 : 2 in Zn(II) and Cd(II) complexes. The +1 oxidation state of copper in its metal complexes is evidenced by spin pair diamagnetic nature of the complex. It is further confirmed by the fact that 1 g atom of copper in the complex reduces 1.001 equivalent of iron.

Bonding sites of the ligand and probable structures of its complexes are elucidated by comparison of ir spectra of the metal-complexes with that of the ligand which can exist in thiol or thione form (I, a – c). IR spectrum of the ligand reveals thioamide bands (due to NCSH or HNCS group) and bands around 2500 and 750 cm^{-1}, which correspond to ν_{S-H} and ν_{C-S}. This confirms the existence of

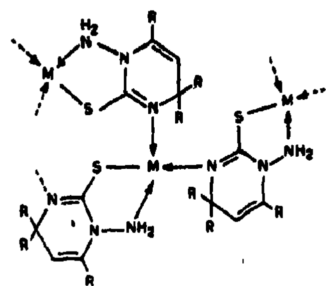
tautomeric forms. In other words, the double bond in thioamide group is delocalized as shown in I(c).

TABLE 1—ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE METAL COMPLEXES WITH THE LIGAND 1-AMINO-4,4,6-TRIMETHYL-1H,4H-PYRIMIDINE-2-THIOL

	Analysis(%)					Colour
	C	H	S	N	Metal	
AgL	30 41	4 20	15 40	11.20	38.92	Yellowish white
	(30 23)	(4 32)	(15 11)	(11.52)	(38 0)	
CuL	35 70	5 24	18.10	13.51	27 40	White
	(35.97)	(5 14)	(17 98)	(13 71)	(27.21)	
TlL	22 68	3 28	11 11	8 70	54 16	Yellowish white
	(22.44)	(3 20)	(11 21)	(8 54)	(54 58)	
ZnL_2, H_2O	39 86	6 10	19 72	15 40	15 18	White
	(39.68)	(6 14)	(19 85)	(15 12)	(15 45)	
CdL_2	37.0	5 46	18.20	14 40	24 60	White
	(37 14)	(5 31)	(18 57)	(14.15)	(24 48)	
$Hg_2L_2Cl_2$	20 90	2 85	10.21	7 64	49 65	Yellowish white
	(20.68)	(2 96)	(10 31)	(7 88)	(49 40)	

L represents ligand Figures within the parentheses are Calcd values

The ligand contains three donor sites, *viz.*, N of amino group, N of pyrimidine ring and S of thione (thiol) group. Coordination of metal ions through N of amino group and S results in the formation of five membered ring and is probably the most favoured arrangement. The absence of a band around 2500 cm^{-1} (due to ν_{S-H}) in the spectra of all metal complexes indicates the deprotonation of thiol group and formation of metal-sulphur bond. Appearance of new bands around 350 cm^{-1} in the spectra of complexes confirms the formation of this bond. Bonding of metal with S will localize the charge between N and C of thioamide group which was otherwise delocalized among N, C and S [structure I(c)]. The complexation will thus result in the shifting of ir band due to ν_{C-N} towards higher wave numbers and band due to ν_{C-S} towards lower wave numbers. Thioamide bands having major contribution from ν_{C-N} and appearing around 1300 cm^{-1} in the spectrum of the ligand, shift by about 65 cm^{-1} towards higher wave number side in the spectra of the complexes. The band around 750 cm^{-1}, which is mostly due to ν_{C-S}[7] in the spectrum of the ligand, shifts by about 65 cm^{-1} towards lower wave number on complexation and supports the formation of metal-sulphur bond. In case of Cu(I), Ag(I) and Tl(I) complexes, the blue shift observed in thioamide band around 1300 cm^{-1} is, however, small (~25 cm^{-1}). This may be due to its partial compensation with the red shift, occurring due to interaction of ring N with metal atoms (which takes place as a result of polymer formation). Based on these facts, appearance of new bands around 400 cm^{-1} (due to metal-nitrogen interaction) and known preferences of Cu(I), Ag(I) and Tl(I) complexes for tetrahedral structure[8], the polymeric structure (II) can be proposed for the metal complexes.



M = Cu, Ag or Tl

R = CH_3

(II)

The insolubility of these complexes supports the polymeric nature. However, Tl-complex is soluble in boiling water. This may be attributed to the weaker Tl – N bonds which is expected on the basis of its pronounced class 'b' behaviour[9-11]. At higher temperature, the interaction of ring N seems to be broken resulting in a soluble monomer. IR spectral results and stoichiometry (1 : 2) indicate tetrahedral coordination[8] of Zn(II) and Cd(II) in their complexes. Monomeric nature is also supported by the partial solubility of these complexes in water (boiling). According to elemental analyses, the Zn-complex contains water molecule. However, a band around 880 cm^{-1}, characteristic of coordinated water, is not observed in the ir spectrum of the complex. It may thus be assumed that the water molecule is lattice held.

The stoichiometry HgLCl, occurrence of $\nu_{Hg-Cl-Hg}$ (bridging) modes at 260 and 245 cm^{-1}, absence of a strong ν_{Hg-Cl} (terminal) band[12-14] at 300 cm^{-1} along with the given ir spectral results can be interpreted by the dimeric structure of mercury complex, in which Hg(II) is tetrahedrally coordinated.

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Ternary Complex—Influence of Oxalic Acid on Vanadium(V) Determination with 4-Sulpho-2-Aminobenzenethiol in Aqueous Solution

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Vanadium(V) forms a ternary blue violet complex with oxalic acid and 4-sulpho-2-aminobenzenethiol. The complex is formed in the concentration range of 0 24 M to 0.64 M hydrochloric acid. It absorbs maximum at 560 nm and is stable for 5 hr at room temperature. The system obeys Beer's law from 1 to 36 ppm The molar absorptivity and Sandell's sensitivity values are $1\ 6 \times 10^3$ $l.mole^{-1}cm^{-1}$ and 0.0302μg cm^{-2} V(V). A 50-fold excess of Co(II), Ni(II), Mn(II), Zn(II), Cd(II), Bi(III), Sn(II), Pb(II), Tl(IV), Mo(VI), W(VI), U(VI) and tartrate, fluoride, acetate, citrate, EDTA, oxalate do not interfere. The mixed-ligand complex is formed in 1 : 1 : 1 ratio of V : oxal : thiol. The overall stability constant of the vanadium complex is 6.40 at 29±1° The photometric method has been found to be very selective in presence of titanium(IV) and other metal ions. Iron(III) and iron(II) strongly interfered

A number of aryl hydroxamic acids[1-4] have been used as analytical reagents for the estimation of vanadium in materials and matrices. The formation of vanadium complexes of variable composition at varying conditions of *p*H and acidities[5] indicated the potential complexing power of the reagents. The selectivity of the methods described earlier in a review[6] and a monograph[7] is limited due to interferences by iron(III)/iron(II) and titanium(IV) The tolerance limits with sequestering agents and prior separation are not effectively high enough. Some ternary procedures provide very high sensitivity, but are less selective for the separation and determination of vanadium(V) in presence of small amounts of Ti(IV). The use of oxalic acid as the mixed ligand component for vanadium determination by the ternary procedure involving either solvent extraction or aqueous medium are not reported earlier.

Oxalic acid, which forms 5-coordinate neutral oxalate complexes, acts as a bidentate ligand to give a ternary complex reported in this paper. It reacts with many transition metal ions such as Hg(II), Pd(II), Cr(VI), Os(VIII) to give useful analytical methods of determination. Vanadium(V) has been determined in purely aqueous medium with high selectivity and without the use of any reducing agent. Selective complex formation and masking action of oxalate ion is the basis of a spectrophotometric method of determination in presence of excess of Ti(IV) and other ions, but iron(III) strongly interferes.

Experimental

Apparatus: A Hilger Uvispek spectrophotometer with 1 cm glass cells was used for absorbance measurements A Perkin-Elmer IR spectrophotometer was used for recording the ir spectra of the reagent

Reagents Ammonium vanadate (E. Merck) was dissolved in water containing a few drops of ammonia and standardized to give 0.1 mg/ml solution of the metal[7,8]. Solutions of diverse ions were prepared from their analytical grade salts. All other chemicals and solvents were of A. R. quality.

4-Sulpho-2-aminobenzenethiol: Distilled 2-aminobenzenethiol was sulphonated[9,10] by slow and dropwise addition to sulphuric acid at 5°. The mixture was stirred thoroughly for 30 min and the thick mass was added to ice-water. The compound was recrystallized to give needle-shaped crystals (m p. 190°) 1 0% aqueous solutions of reagent and oxalic acid were used for the ternary system.

General procedure: An aliquot of standard vanadium(V) solution was mixed with 5 ml of 1.0% reagent solution, 5 ml of 1.0% oxalic acid and 2 ml of 4 *M* hydrochloric acid in a 25 ml volumetric flask. The mixture was kept for half-an-hour with occasional shaking. The volume was made up with double distilled water. The reaction mixture was mixed thoroughly at room temperature. The reagent blank prepared similarly showed no absorbance. The absorbance of the blue-violet complex was measured at 560 nm against water blank.

Results and Discussion

Absorption spectrum: Both the binary and ternary complex systems showed similar absorption in the visible region. The ternary complex (violet)

* Contribution made during the tenure (1974-77) in the Scientists Pool of C.S.I.R., New Delhi.

absorbs maximum at 560 nm when measured against water blank (Fig. 1).

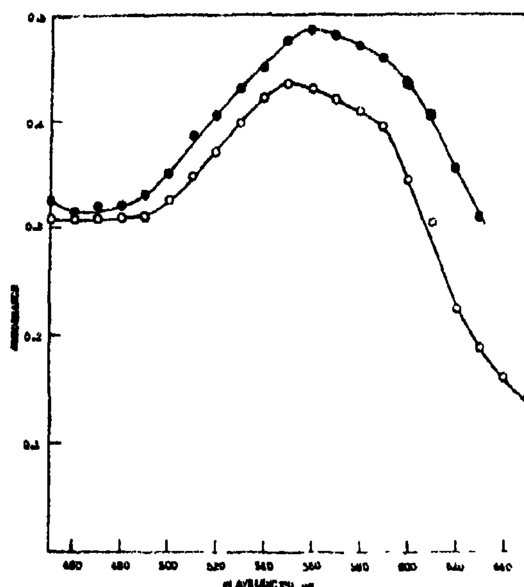


Fig. 1. Absorbance curve.
O Binary complex, 16 ppm
● Ternary complex, 16 ppm.

Effect of acidity, reagent, time : The complex is formed at *p*H from 2.0 to 2.5. A flat maximum at 510-540 nm is obtained between *p*H 1.0 and 2.0 The complex is fully formed when the HCl concentration lies between 0.24 *M* and 0.64 *M*. 2 ml of 4*M* HCl was added for all measurements and the acid concentration was maintained at 0.32 *M* HCl.

It was found that 4-9 ml of 1.0% oxalic acid is sufficient for complete formation of the complex with 5 ml of 1.0% reagent. The colour is fully developed by using 0.1 to 10 ml of 1.0% oxalic acid. For a second series of solutions [V(V), 16 ppm] with 5 ml of 1.0% oxalic acid always added to it, the complex begins to form after the addition of 0.1 ml of 1.0% sulpho-thiol reagent. 2 ml of the reagent is sufficient for full colour development. A 5 ml of 1.0% reagent solution was always used. The ternary complex formation is independent of the order of addition of reagents.

Calibration curve, optimum range, photometric error and sensitivity · The system obeys Beer's law from 1-36 ppm of V(V). The optimum range of determination obtained by Ringbom's plot[11] was found to be 4-26 ppm. The per cent relative analysis error per 1% absolute photometric error was obtained following Ayres' equation[18] as 2.7%. The molar absorptivity of the ternary violet complex is 1.6×10^{8} l.mole^{-1} cm^{-1} and Sandell's sensitivity[18] was calculated to be 0.0302 μg cm^{-2} V(V), respectively, at 560 nm.

Composition of the ternary complex : In most of the mixed-ligand systems a log-log method is found necessary to determine the metal to ligand ratios in the complex[14]. In this particular system, the metal : ligand composition was directly determined in a complementary mixture of 12 ml volume. The V(V) : oxal ratio was determined using three different amounts (4, 6 and 8 ml) of an equimolar solution of reagent (R_2) as the fixed component. The complex was formed utilizing equimolar solutions (9.815×10^{-8} *M*) of vanadium(V) and oxalic acid (R_1) following the procedure at 560 nm and 570 nm. The plots of absorbance against $M/(M+R_1)$ fraction of the metal showed a break at 1 : 1 ($M : R_1$) ratio (Fig. 2). Similarly, V(V) : sulpho-thiol ratio was determined using 12 ml mixture of equimolar solutions (9.815×10^{-8} *M*) of vanadium(V) and

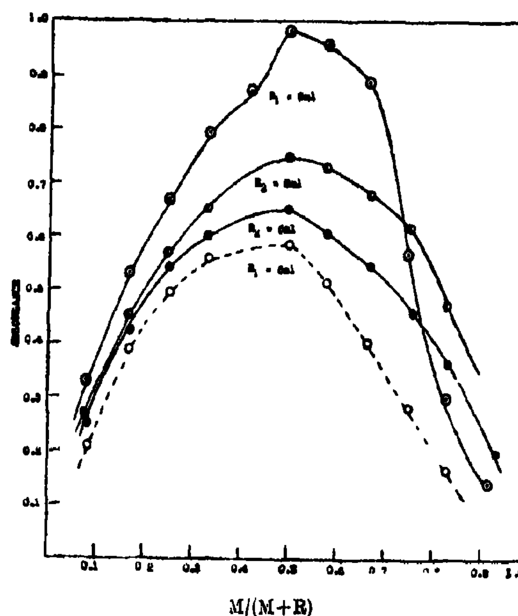


Fig 2 Continuous variation method.
$[M]=[R_1]=[R_2]=9.815\times10^{-8}M$
O $R_1=6$ ml ◐ $=8$ ml ● $R_2=6$ ml ◑ $=8$ ml

reagent (R_2) and correspondingly three varied amounts (4, 6 and 8 ml) of an equimolar oxalic acid solution (R_1) as the other fixed component. The plots of absorbance measured at 550-570 nm against $M/(M+R_2)$ fraction of the metal showed a sharp break at 1 : 1 (M · R) ratio (Fig. 2) in all the experiments. Thus, a 1 . 1 : 1 ($M : R_1 : R_2$) composition was obtained for the complex by method of continuous variation. In mole-ratio method, studies with a fixed amount (4, 6 and 8 ml) of oxalic acid and a 12 ml mixture of equimolar solutions (9.815×10^{-8} *M*) of vanadium(V) and reagent (R_2) indicated a 1 : 1 ($M : R_2$) ratio at 550-570 nm (Fig. 3). Similarly, experiments with a fixed amount (4, 6 and 8 ml) of sulpho-thiol reagent and a 12 ml mixture of equimolar solutions (9.815×10^{-8} *M*) of vanadium(V) and oxalic acid (R_1) indicated a 1 : 1 ($M : R_1$) ratio at 550-570 nm (Fig. 3). The composition of the ternary complex ($1 : 1 : 1 = M : R_1 : R_2$) was verified by the mole-ratio method and

its formula may be assigned as $VO(C_2O_4)$-$(C_8H_8N_2O_6S_2)$.

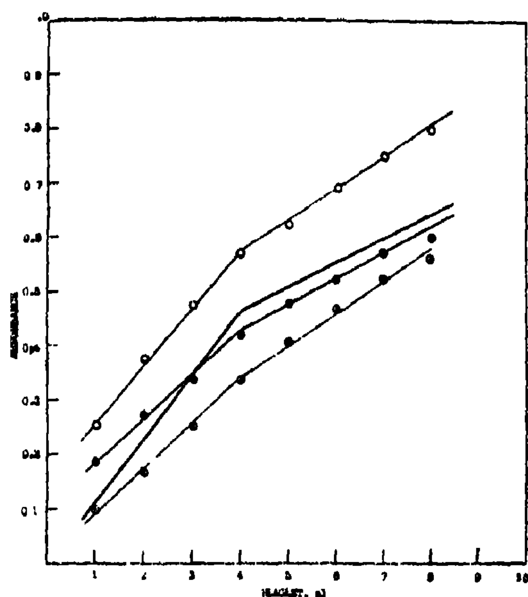


Fig 9. Molar-ratio method
$[M]=[R_1]=[R_2]=9.815\times10^{-4} M$
— $R_1=4$ ml, ○ $R_1=6$ ml,
● $R_2=4$ ml, ○ $R_2=6$ ml

Interference study: The tolerance limits with 0.2 mg of vanadium(V) were determined with 10 mg of diverse ions following the procedure at 0.32 *M* hydrochloric acid. 10 mg of Co(II), Ni(II), Mn(II), Sn(II), Pb(II), Zn(II), Al(III), Bi(III), Zr(IV), Ta(V), Mo(VI), W(VI), U(VI) or Cr(III) showed no interference. 5 mg of Cu(II), Cd(II), Re(VII), Ce(IV), Tl(I) or fluoride did not interfere. 10 mg of acetate, phosphate, ascorbate, sulphate, tartrate, citrate, EDTA are tolerated in the determination. Fe(III) or Cr(VI) strongly interferes. Hg(II), Pd(II), Cr(VI), CN^-, SCN^- present in 5 mg amount interfered in the determination. Ti(IV) showed no interference.

Degree of dissociation and stability constants: The formation constants of the ternary complex have been investigated by the photometric technique. The degree of dissociation (α) for log K^{MA}_{MAL} has been calculated from the relation

$$\alpha = A_m (0.690) - A_s (0.395)/A_m (0.690) = 0.4275$$

The stability constant of the complex has been calculated from the relation $K=1/K'=1-\alpha/\alpha^2 c$, where c is the concentration of the complex. Log K^{MA}_{MAL} has been found to be 3.30. Similarly, log K^{ML}_{MAL} has been found to be 3.10 ($\alpha=0.3333$, $c=6.28\times10^{-6}$ *M*). Almost equal stability value points to the simultaneous and successive complex formation in the vanadium chelate. Thus, the overall stability constant has been calculated to be 6.40 (log $K=$ log $K^{MA}_{MAL}+$log K^{ML}_{MAL}) at $29\pm1°$.

The violet ternary complex is extracted with *n*-butyl, *iso*-butyl, *n*-amyl and *iso*-amyl alcohols. Chloroform, benzene and carbon tetrachloride do not extract the complex due to the presence of a sulphonic acid group in the molecule.

No coloured complex is formed by VO(II) either in the presence or absence of oxalic acid. The vanadyl complex has a 5-coordinate structure with vanadyl oxygen at the top of a possible tetragonal pyramidal geometry. The sulpho-thiol reagent behaves here as a mono-protic bidentate ligand. A violet complex separates from the bulk solution after 24 hr at room temperature and is thermally stable.

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Ternary Extraction and Photometric Estimation of Vanadium(V) with N-Cinnamoyl-N-Phenyl Hydroxylamine (N-CPHAmine) and Thiocyanate in Chloroform

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Vanadium(V) forms a ternary system by mixed-ligand complexation with N-cinnamoyl-N-phenyl hydroxylamine and ammonium thiocyanate at pH 0.95. The green coloured complex absorbs maximum at 580 nm and is soluble in chloroform. The method has improved selectivity and has been successfully applied to estimate the amounts of vanadium in alloy steel and ores.

SYNERGIC effect in chelate extractions are often observed in studying mixed-ligand equilibria systems[1-4]. Such complex formation with thiocyanate ion along with N-arylhydroxamic acid leading to a new photometric method of selective separation and determination of vanadium has been described in this paper.

The reagent, N-cinnamoyl-N-phenylhydroxylamine has been found to form a green coloured thiocyanato complex with vanadium in chloroform. The complex absorbs maximum at 580 nm with a bathochromic shift of 50 nm. The molar absorptivity of the complex formed in 0.16 *M* HCl is 7.0×10^{3} l. mole^{-1} cm^{-1} at 580 nm Only Fe(III) and Ti(IV) interfere in the determination. The method has been found to be rapid and simple and finds successful application in high speed steel and ore analysis.

Experimental

Reagents and Solutions : A stock solution of vanadium(V) (2.2 mg/ml) was prepared from G. R. (E. Merck) grade ammonium vanadate and standardized[5]. The reagent N-CPHAmine (158°-161°) was prepared following the method in literature[6]. Standard solution of the reagent was prepared in purified chloroform. All other reagents and solutions of the diverse ions were prepared from Analytical Grade compounds.

Apparatus : A Hilger-Uvispek spectrophotometer was used for all measurements with 1 cm matched glass cells. An Elico *p*H-meter model LI-10 (India) was employed for *p*H measurements.

General procedure : An aliquot of vanadium(V) solution (100 μg) was transfered into a 100 ml separatory funnel, 6 ml of 1% reagent solution and 5 ml of 2% ammonium thiocyanate solution and required volume of chloroform were added to maintain the volume of the organic phase at 15 ml. The acidity was adjusted to 0.16 *M* by the addition of hydrochloric acid. The green coloured complex was extracted by shaking the mixture thoroughly for 7-8 min. The extraction was repeated twice with 5 ml portions of chloroform. The combined extract and washings were dried over anhyd. sodium sulphate, transfered into a 25 ml standard flask and the volume was made up with pure solvent. The absorbance of the extract was measured at 580 nm against a reagent blank. The violet binary complex [V(V) : N-CPHAmine] in the same solvent showed maximum absorption at 530 nm. The wide bathochromic shift of 50 nm in the absorbance maximum indicated that a mixed-ligand complex was formed when thiocyanate ions were present.

Procedure for analysis of steel : The steel sample (0.5 g) was dissolved in 1 : 4 H_2SO_4, heated to fumes after dissolution. It was cooled and made up to a volume of 250 ml with acidulated water. An aliquot (2.5 ml to 8.0 ml) of the above solution was diluted to 15 ml with water, oxidized with potassium permanganate solution. Iron(III) was precipitated out with 15% (w/v) NaOH solution for complete recovery of vanadium(V) as sodium vanadate in the filtrate. The vanadium content was estimated as stated earlier

Procedure for analysis of ilmenite : Finely powdered ilmenite ore (0.5 g) mixed with 9 g of potassium bisulphate was heated and brought to a clear melt. The product was cooled and leached with dil H_2SO_4 containing HNO_3. The mixture was heated and iron(III) and other metals were removed as hydroxides by adding NaOH solution. The volume of the filtrate was made up to 100 ml. The vanadium content was estimated as before.

Results and Discussion

Effect of N-CPHAmine reagent and ammonium thiocyanate : Extractions of the ternary complex in

TABLE 3—DETERMINATION OF VANADIUM(V). VANADIUM CONC IN THE EXTRACT 4 μg/ml, ABSORBANCE MEASURED AT 560 nm IN PRESENCE OF DIFFERENT IONS

Ions	Added as	Tolerance limits, ppm	Ions	Added as	Tolerance limits, ppm
Oxalate	Oxalic acid	100	Cr(III)	$Cr(NO_3)_3$	100
Tartrate	Tartaric acid	200	Mn(II)	$MnCl_2$	300
Citrate	Na-citrate	1000			
EDTA	Na_2-EDTA	500	Co(II)	$CoCl_2$	70
Fluoride	NaF	200	Ni(II)	$NiCl_2$	125
			Cu(II)	$CuCl_2$	200
Acetate	Na-acetate	3200	Zr(IV)	$Zr(NO_3)_4$	200
Phosphate	$(NH_4)_2HPO_4$	2400	Th(IV)	$Th(NO_3)_4$	300
Zn(II)	$ZnSO_4$	200			
Cd(II)	$CdCl_2$	200			
Hg(II)	$Hg(NO_3)_2$	200	Re(VII)	$KReO_4$	70
Pb(II)	$Pb(NO_3)_2$	200	Mo(VI)	$(NH_4)_2MoO_4$	125(EDTA)
Ca(II)	$CaCl_2$	500	W(VI)	Na_2WO_4	60
Pd(II)	$PdCl_2$	250	UO_2(II)	$UO_2(NO_3)_2$	75
Al(III)	$Al(NO_3)_3$	200			

presence of an excess of thiocyanate [5 ml of 2% (2.6×10^{-3} *M*) solution] and different volumes of 1% (w/v) (4.2×10^{-4} *M*) solution of N-CPHAmine reagent showed that extraction was quantitative when 6 ml of the reagent was used.

Beer's law, optimum range, photometric error, molar absorptivity and sensitivity: The ternary system obeyed Beer's law from 0.4 to 12 μg/ml of V(V). The optimum concentration range as obtained from steepest portion of Ringbom's plot[7] is found to be 1-8 μg/ml of the metal (Table 1). The photometric error according to Ayre's equation[8] was 2.72%. The molar absorptivity of V(V)-N-CPHA-SCN complex in chloroform was calculated from Beer's law to be 0.70×10^4 l. mole^{-1} cm^{-1}. The Sandell's[9] sensitivity for reaction is 0.0075 μg/cm^2 of V(V).

TABLE 1—ESTIMATION OF VANADIUM(V)-CPHAMINE-THIOCYANATE IN ACID MEDIUM AT 580 nm

V(V) Taken, ppm	V(V) Found, ppm	% Error
0 4	0 39	2 5
0 8	0 78	2 5
1 0	0 98	2 0
2 0	1 95	2 0
3 0	3 01	0 3
4 0	3 98	0 5
6 0	5 90	1 7
8 0	7 85	1.8
10 0	9 80	2 0
12 0	11 7	2 5

Analysis of alloy steel and ilmenite ore samples A standard high-speed steel (Sample No. BAS-64b) was obtained from the Bureau of Analysed Samples Ltd., Newman Hall, Yorkshire, U. K. and ilmenite ore of Hornbendite rock from Kavur Anchal, Tamilnadu, India, was obtained by courtesy of the Geological Survey of India, Calcutta. Three repeatitive extractions were carried out for each of the alloy-steel and ore samples and the V content was found in each case. The average result is being given in the Table 2.

TABLE 2—VANADIUM CONTENT OF STANDARD SAMPLES

Alloy steel		Ilmenite ore	
%Reported	%Found	%Reported	%Found
1 99	1 96	0 1	0 094

Interference studies · The effect of foreign ions in the determination of vanadium by ternary extraction is given in Table 3 A deviation by 0.005 absorbance from that expected for 4 μg V/ml of the final extract is considered the limit of tolerance. A 50 fold excess of urea and thiourea have been tolerated. Fe(III), Ti(IV), Nb(V) and Ta(V) interfere. Mo(VI) has been tolerated at 50 times excess over vanadium(V) in presence of EDTA as complexing agent. The method has been found to be selective in presence of 50 times excess of a large number of transition metal ions and 25 to 100 times excess of a few anions. All other ions investigated for this ternary extraction have considerably higher tolerance limits.

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Yield of Molecular Hydrogen as a Criterion for the Radiation Stability of Organic Compounds*

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The fate of *n*-hexane molecule labelled by hot recoiling tritium atom was experimentally studied in liquid and solid phases, with and without iodine (5×10^{-4} *M*) as thermal free radicals scavenger. The addition of such micro amount of iodine did not appreciabily reduce the yields of tritium-labelled hot interaction products. So is the case with light hydrocarbons. The same amount of iodine had no effect upon these yields in the solid state. Tritium-labelled ethylene yield has therefore been taken as a measure of the degree of stability of labelled and excited *n*-hexane molecule. The yield of C_2H_3T was small to indicate that >90% of n-$C_6H_{13}T$ and HT are formed in the hot region of interaction between T atom and *n*-hexane molecule; the interaction is too fast to allow displacement of one hydrogen atom by *one tritium one or the abstraction of the first by the second to be significantly* affected by a third object like iodine. The "residual" excitation energy in *n*-hexane-T molecule is too small and does not cause its disintegration. The yield of labelled ethylene product is very small and indicates that very few highly excited n-$C_6H_{13}T$ molecules disintegrate immediately after formation. Formation of HT and n $C_6H_{13}T$ molecules follows different mechanisms. Hence HT yield could not serve as a measure for the stabilization and survival of n-$C_6H_{13}T$ molecules, since the first does not form at the expence of the second.

IT has been stated that the yield of molecular hydrogen as a radiation product serves as a good measure of the extent to which an organic compound can withstand the action of ionizing or electro-magnetic radiation[1-6]. The same idea was wrongly transferred to the field of hot atom chemistry which is very close to radiation chemistry. As a result, scientists started talking about a molecular hydrogen of the form HT instead of H_2.

The principal aim of this research was to demonstrate experimentally that the yield of labelled olefines (but not HT) is the real measure of the extent to which *n*-hexane molecule survives after getting labelled by one tritium atom.

Experimental

Detectors : A conventional radio gas chromatography system was used[7,8,9]. It consisted of two detectors :

(i) a gas flow proportional counter which registered β radiation passing through it with the carrier gas (helium). The corresponding β energy spectrum was converted to peaks. The area of each peak is proportional to the total activity of the corresponding compound labelled by tritium atom ;

(ii) the second detecting system being an ordinary cathatometer with sensitive thermisters.

Columns : To carry out analysis of liquid-phase products, a 4-meter copper column 5 mm i.d. was used. It was packed with diatomite (0.25-0.50 mesh) coated with 10% w/w dioctylphthalate as the stationary phase. Oven temperature was $80\pm1°$. Helium was the carrier gas.

Analyses of gas-phase products were carried out with 2 or 4 meter (5 mm i.d.) copper columns packed with silica gel at different temperatures (room, 100 and 200°).

Irradiation Two fluxes of thermal neutrons were used ·

(i) Liquid-phase samples : a thermal flux of 1.2×10^{13} neutrons/sec/cm^2 at 70°. Time of irradiation, 15 min.

(ii) Solid-state samples : a thermal flux of 9×10^{11} neutrons/sec/cm^2 at $-170°$. Time of irradiation, 2 hr.

Source of neutrons : A nuclear reactor type ERT – 1000.

Samples. 20 μl samples of *n*-hexane were placed in 4 cm long and 3 mm diameter quartz ampoules along with 20 μg lithium carbonate. Ampoules were evacuated (10^{-4} torr) after being frozen in liquid nitrogen (–196°) and sealed with the aid of an oxygen flame.

Results and Discussion

To discuss the main question of the stabilization of tritium labelled organic compounds in liquid state, and the role and the nature of the second constituent, it is important to note that the

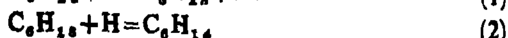
* This work was done at the Department of Radiochemistry, Moscow State University, Moscow, USSR.

yield of HT gas, as the major product in most cases, cannot serve as an evidence for the presence of any kind of "protection" of one molecule over the other.

This is true since the formation of a large part of HT gas takes place by a fast single-step abstraction of one hydrogen atom by a hot tritium atom (having a high kinetic energy) resulting in the instantaneous evolution of HT molecule[10,11].



$$C_6H_{14}+T=C_6H_{13}+HT \quad (1)$$



$$C_6H_{13}+H=C_6H_{14} \quad (2)$$

This process takes place so fast that nothing can affect its occurrence. There is a total agreement on this.

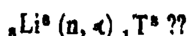
Yield of HT gas from *n*-hexane was 53.4% (Table 1). At least 90% of this yield was formed by this mechanism.

TABLE 1—PERCENT YIELD OF TRITIUM LABELLED PRODUCTS

	HT	C_1-C_5	*n*-hexane-T	light polymer-T	heavy polymer-T
liquid phase	53.4	10.7	28.9	2.5	4.5
liquid phase+ iodine	51.2	10.2	26.9	7.9	3.8
solid phase with and without iodine	45.6	14.3	33	2.7	4.1

What is therefore the alternative criterion which might be taken as a measure for the stability and for the defending (protecting) effect as well? It is the yield of the original irradiated system itself labelled by tritium and the total yield of labelled C–C bonds rupture taking place in the labelled parent molecule ($C_6H_{13}T$)

What happens to a *n*-hexane molecule just labelled by a hot tritium atom formed as a result of the nuclear reaction

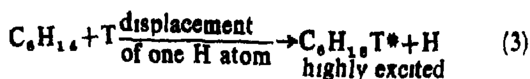


$$_3Li^6\,(n,\alpha)\,_1T^3\ ??$$

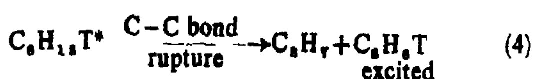
Once tritium atom is in the hot stage at the instant of the reaction, the interaction of tritium with *n*-hexane molecule should take place by the fast single-step displacement of one hydrogen atom giving rise to an excited *n*-$C_6H_{13}T$ molecule. Such a molecule either stabilizes* or decomposes.

Decomposition of an excited n-$C_6H_{13}T$ molecule C–C bond breakage :

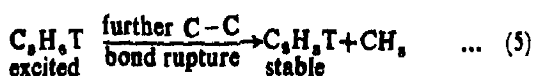
The decomposition can occur via the following possible route :



$$C_6H_{14}+T \xrightarrow[\text{of one H atom}]{\text{displacement}} \underset{\text{highly excited}}{C_6H_{13}T^*+H} \quad (3)$$



$$C_6H_{13}T^* \xrightarrow[\text{rupture}]{\text{C–C bond}} C_3H_7+\underset{\text{excited}}{C_3H_6T} \quad (4)$$



$$\underset{\text{excited}}{C_3H_6T} \xrightarrow[\text{bond rupture}]{\text{further C–C}} \underset{\text{stable}}{C_2H_3T}+CH_3 \quad \dots (5)$$

* HT and *n*-hexane-T yields comprise 80-82% of the total labelled products in the liquid phase (Table 1).

Unlabelled parafines can be formed according to the following radical recombination processes :



$$C_3H_7+H \quad =C_3H_8 \quad \dots (6)$$



$$CH_3 \ +C_3H_7=C_4H_{10} \quad \dots (7)$$



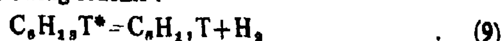
$$CH_3 \ +H \quad =CH_4 \quad \dots (8)$$

Olefines :

Olefinic products seem to be the sole products of any disintegration process of an excited hexane molecule caused by C–C bond breakage. In other words, neither HT nor labelled parafinic compounds help as a measure of the stability of this excited molecule.

Other types of decompositions :

Our separation conditions and many other considerations did not allow for a full tracing of labelled hexane ($C_6H_{11}T$). This product might be a consequence of a stabilization process of a labelled and excited hexane molecule by the liberation of one hydrogen molecule[6,12] according to the following scheme.

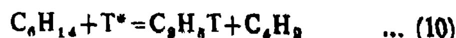


$$C_6H_{13}T^*=C_6H_{11}T+H_2 \quad . \ (9)$$

Therefore C–C bond rupture model remains the unique stability criterion

Our gas-phase assay did not show any evidence of the presence of light labelled olefines such as propene or butene though susceptibility of the set up and column conditions were absolutely capable to detect any trace of them.

Formation of labelled parafines should, therefore, be a sequence of a substantially different mechanism. This mechanism must be relatively easier since C_1–C_5 labelled parafines were always detected in all experiments. The following mechanism accounts for the formation of such products :



$$C_6H_{14}+T^*=C_2H_5T+C_4H_9 \quad \dots (10)$$



$$C_4H_9 \ +H=C_4H_{10} \quad . \ (11)$$



$$\text{or} \quad C_6H_{14}+T^*=C_4H_9T+C_2H_5 \quad (12)$$



$$C_2H_5 \ +H=C_2H_6 \quad . \ (13)$$

abstraction of an alkyl group by a hot tritium atom as a result of a fast localized attack at a C–C bond with the immediate formation of either the lighter alkane (CH_3T) or the heavier one ($C_5H_{11}T$). Table 2 shows that yields of CH_3T and of C_2H_5T are 3.5 and 2 times that of $C_5H_{11}T$ respectively.

TABLE 2—PERCENT YIELD OF C_1-C_5 LABELLED HYDROCARBONS

	CH_3T	C_2H_5T	C_2H_3T	C_3H_7T	C_4H_9T	$C_5H_{11}T$	Total
liquid phase	3.77	1.93	0.56	1.29	2.12	1.01	10.7
liquid phase+ iodine	3.9	1.64	0.22	1.87	2.74	0.91	10.9
solid phase with and without iodine	4.65	2.32	0.55	1.07	3.58	2.19	14.3

Moreover, radicals such as C_2H_6T (step 4) can combine with a free hydrogen radical $H^{\cdot}$ to form the corresponding alkane :

$$C_2H_6T + H^{\cdot} = C_2H_7T \qquad \ldots (14)$$

This suggests that the moderately excited radical C_2H_6T cools down after several collisions with different surrounding species. As a result, it loses the excess energy of excitation (which could be vibrational or rotational in this stage) and thus survives rather than decomposes. This could be a further explanation of the previous question of why did labelled alkanes were always formed in considerable amounts, while just one labelled alkane (ethylene) was detected in our circumstances (Table 2).

Conclusions :

1. There is no way to avoid the formation of HT gas from a "hot" interaction of tritium with hexane molecule. The exact percentage yield of $C_6H_{12}T$ which undergoes disproportionation is unknown, since the addition of iodine ($5 \times 10^{-3} M$) reduced the yield of hexane-T very slightly (about 4%). This would imply that a very small part of hexane-T was formed by the addition of thermal tritons most likely to C_6H_{13} radicals left after the direct formation of HT.
2. Difference between types of interactions of different bombarding radiations (γ, fast electrons, and thermal neutrons for instance) should be taken into consideration. Nature of each kind of radiation inevitably gives rise to different modes of interactions.
3. Labelled olefines are the sole measure for the stability of an excited and tritium labelled *n*-hexane molecule.

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Physico-chemical Studies on the Composition and Stability Constants of Zn(II), Cd(II) and Hg(II) DL-Valine Complexes

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DL-Valine [$(CH_3)_2CH\,CH(NH_2).COOH$] complexes of divalent Zn, Cd and Hg have been investigated potentiometrically in aqueous 0.1 *M* $NaClO_4$ solution using Bjerrum-Calvin technique as modified by Irving and Rossotti at 20, 30 and 40°. The refinement of stability constants was made by the method of least square. The trend in the stability of these 1 : 1 metal complexes has been found to be :



Zn(II) > Hg(II) > Cd(II).

Cd(II) forms only 1 : 1 complex at *p*H 3.35-8.55 and Zn(II) and Hg(II) 1 : 1 and 1 : 2 complexes at *p*H 2.90-8.20 and 3.40-7.75, respectively. The overall changes in thermodynamic parameters, ΔG, ΔH and ΔS, accompanying the complex formation have been determined.

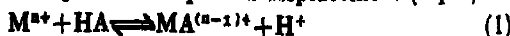
SAXENA and co-workers[1-3] have studied metal complexes of amino acids which have found useful application in biological and pharmaceutical fields[4]. The present communication describes the chemistry of Zn(II), Cd(II) and Hg(II) complexes with DL-valine, their composition, stability constants and thermodynamic functions, accompanying the complexation reactions at different temperatures.

Experimental

DL-Valine [$(CH_3)_2.CH.CH(NH_2).COOH$], referred herein as HA, was obtained from B D. H., Poole, England. All other chemicals were of AnalaR grade. Solutions of metal ions were prepared in doubly distilled carbon dioxide free water. The experimental procedures were the same as reported earlier[1-3]. *p*H measurements were made on 'EC' *p*H meter (5651) with glass calomel electrode assembly in a nitrogen atmosphere. The temperature of the cell was maintained by thermostat (U_3 type, German) having an accuracy of ±0.1°.

Results and Discussion

Stoichiometry : The composition of the complex formed during the interaction of metal ions with DL-valine was established by measuring the magnitude of proton displacement during the titration of ligand in the absence and presence of metal ion at different ratios (Fig. 1) indicating the complex formation which results in the lowering of buffer region due to proton displacement (Eq. 1).



$$M^{n+} + HA \rightleftharpoons MA^{(n-1)+} + H^+ \qquad (1)$$

where M^{n+} stands for Zn(II), Cd(II) and Hg(II).

When metal ion and ligand are mixed in the ratios 1 : 4, 1 : 2 and 1 : 1, the inflections are obtained at m=0.5, 1.0 and 2.0 respectively (m being the mole of NaOH per mole of HA). These inflections suggest the formation of MA^+ and MA_2 corresponding to 1 : 1 and 1 : 2 complexes respectively with considerable overlapping according to the following equations :

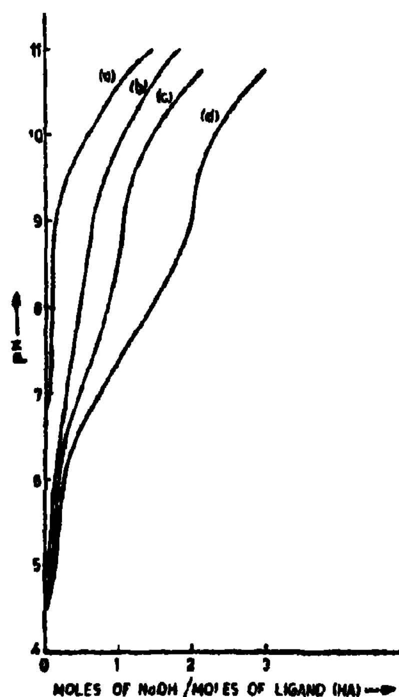


Fig 1 Potentiometric titrations of DL-valine (HA) in the absence and presence of Hg(II) with 0.1 *M* NaOH.

Curve (a) . 4 0 m*M* HA
Curve (b) 4.0 m*M* HA + 1 0 m*M* Hg(II)
Curve (c) 4 0 m*M* HA + 2.0 m*M* Hg(II)
Curve (d) 4 0 m*M* HA + 4 0 m*M* Hg(II)





$$M^{2+} + HA + OH^- \rightleftharpoons MA^+ + HOH \qquad (2)$$

$$MA^+ + HA + OH^- \rightleftharpoons MA_2 + HOH \qquad (3)$$

$$M^{2+} + 2HA + 2OH^- \rightleftharpoons MA_2 + 2HOH \qquad (4)$$

i.e. 1 : 1 and 1 : 2 complexes are formed simultaneously.

Stability constants : Stability constants of DL-valine [$(CH_3)_2CH.CH(NH_2).COOH$] complexes with divalent Zn, Cd and Hg were determined using Calvin-Bjerrum[5,6] technique as modified by Irving and Rossotti[7] and further refined by least square treatment.

At any pH, the value of free ligand concentration [A] was calculated from the relation (Fig. 2)

$$[A] = \frac{[Ligand]_{total} - [ligand]_{bound}}{(H^+/K_a)+1} \quad (5)$$

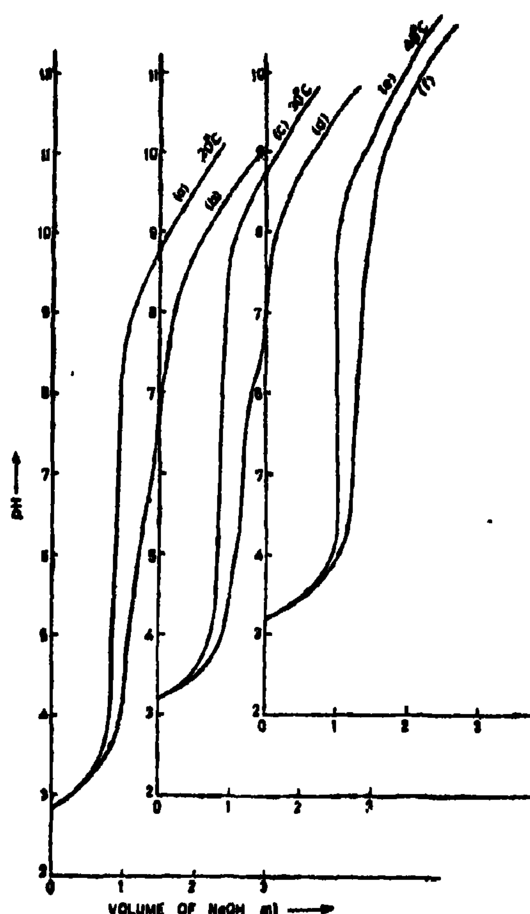


Fig 2 Potentiometric titrations of DL-valine (HA) in the absence and presence of Hg(II) with 0 1 M NaOH

Curve a, c and e : 0.1 M $NaClO_4$+4.0 mM $HClO_4$+4.0 mM HA at 20, 30 and 40°, respectively.

Curve b, d and f . 0.1 M $NaClO_4$+4 0 mM $HClO_4$+4 0 mM HA +1.0 mM Hg(II) at 20, 30 and 40°, respectively

where K_a, the dissociation constant[8] of HA, is 3.235×10^{-10}. The values of log K_1 and log K_2 were obtained from the formation curves (Fig. 3) at $\bar{n}$=0.5 and 1.5 respectively.

The constants are best evaluated by the least square method

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} K_1K_2 - K_1 \quad \ldots (6)$$

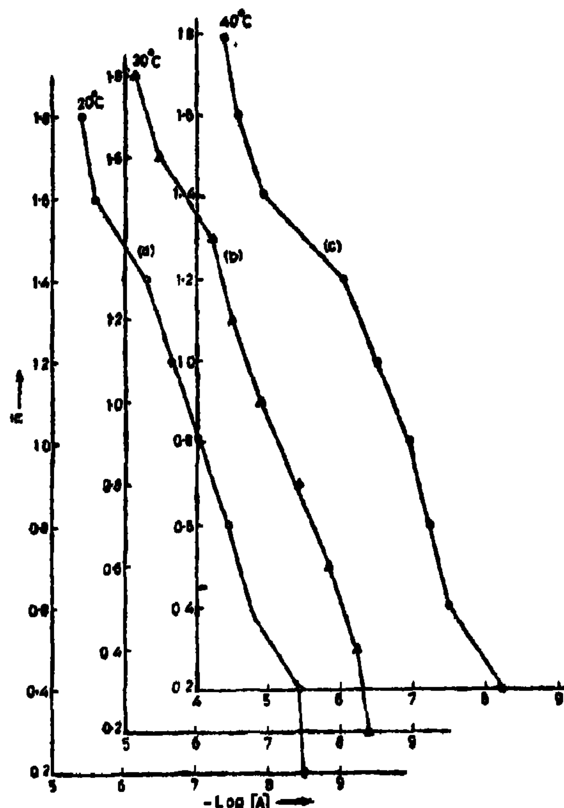


Fig 3 Formation curves at 20, 30 and 40° for Hg(II) complexes of DL-valine (HA)

Curve a at 20°
Curve b at 30°
Curve c at 40°

The values of stability constants at various temperatures and by different methods are summarised in Table 1.

Thermodynamic functions : The values of overall changes in free energy, ΔG, enthalpy, ΔH, and entropy, ΔS, accompanying complex formation have been determined using the standard equations.

$$\Delta G = -RT \log \beta \quad (7)$$

$$\Delta H = \frac{2.305\ R\ T_1T_2 \log K_2/\log K_1}{(T_2-T_1)} \quad (8)$$

and

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (9)$$

The values of thermodynamic parameters are given in Table 1.

Discussion

From a comparative account of the stability constants, it is evident that the values are slightly higher at 20° as compared to 30° and 40°, indicating that low temperature is favourable for complex formation. The trend in the stability of metal complexes is Zn(II) > Hg > Cd(II) in the case of

TABLE 1—METAL LIGAND STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS FOR Zn(II), Cd(II) AND Hg(II) COMPLEXES OF DL-VALINE

System	Temperature °C	Bjerrum method		Least square method		ΔG	ΔH	ΔS
		$\log K_1$	$\log K_2$	$\log K_1$	$\log \bar{K}$	KJ mol^{-1}	KJ mol^{-1}	(e u)
	20	8.90	4.50	8.92	4.40	−74.5	—	—
Zn-HA	30	8.35	4.15	8.41	4.15	−72.2	−241.2	−188.9
	40	7.35	3.85	7.38	3.84	−66.6	—	—
	20	7.25	—	7.81	—	−43.4	—	—
Cd-HA	30	6.75	—	7.56	—	−43.4	−122.4	−62.3
	40	6.20	—	6.88	—	−40.8	—	—
	20	8.05	5.95	8.06	5.96	−77.9	—	—
Hg-HA	30	7.00	5.80	7.94	5.82	−79.0	−205.2	−99.5
	40	7.35	4.80	7.34	5.28	−74.9	—	—

Uncertainty limit for $\log K_1 = \pm 0.4$ and $\log K_2 = \pm 0.3$, for thermodynamic functions $\Delta G = \pm 0.3$ KJ mol^{-1}, $\Delta H = \pm 0.5$ KJ mol^{-1} $\Delta S = \pm 4.5$ e.u.

1 : 1 which is in agreement with the accepted view that the stability of metal complexes depends on metallic nuclear charge (atomic number), its radius, and the screening effect of the electron present

$$P = A \frac{Z-S}{r} \qquad (10)$$

where P is a polarising action of the metal ion, A is a proportionality coefficient, Z is the atomic number, S is the screening constant and r is the ionic radius.

The complex formation is a spontaneous process which is evident from the negative values of ΔG; the negative values of ΔH also ensure that the reaction is exothermic.

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Kinetics of Oxidation of Glycollic Acid by Quinquevalent Vanadium in Sulphuric Acid Medium

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The oxidation of glycollic acid by V(V) has been found to be first order both in [oxidant] and [substrate] and second order in $[H^+]$. The acid dependence of oxidation can be expressed by equation $\log k = 1.2 \log [H_2SO_4] - 3.74$. The increase in oxidation rate with increase in $[HSO_4^-]$ at constant $[H^+]$ has also been observed. The thermodynamic parameters have been evaluated. $V(OH)_3^{2+}$ and $V(OH)_2(HSO_4)^{2+}$ have been proposed to be the reactive species out of which the latter one is more reactive. A plausible mechanism with V(V) acting as one electron oxidant involving C–C bond fission in the slow step via free radical formation, has been suggested.

BAKORE and Shanker[1] suggested that in the reaction of glycollic acid with vanadium(V) in perchloric acid medium, vanadium(V) acts as a two electron oxidant involving C–H bond rupture in the slow step. No attempt has been made to study the oxidation of glycollic acid by vanadium(V) in sulphuric acid medium. It was, therefore, thought desirable to undertake a study of oxidation of glycollic acid by vanadium(V) in sulphuric acid medium. The results are reported in this paper.

Experimental

Ammonium metavanadate (Reidel) was dissolved in appropriate concentration of sulphuric acid (B. D. H., AnalaR), to prepare vanadium(V) solution. Other chemicals used were of B. D. H., AnalaR grade. The solutions were standardised by conventional methods.

The solutions of the substrate and the oxidant were equilibrated at desired temperature (±0.05) before being mixed. Oxidation reactions were followed by quenching aliquotes, withdrawn at regular known intervals of time, in excess of ferrous ammonium sulphate solution and back titrating by standard potassium dichromate solution using N-phenyl anthranilic acid as indicator.

Results and Discussion

The kinetic studies were made by taking glycollic acid and sulphuric acid in sufficient excess over vanadium(V) concentration. The rate of disappearance of V(V) was observed to follow the first order kinetics uniformly. The integrated form of first order rate equation was also used to evaluate the pseudo first order rate constants (k).

The plot of $\log k$ vs $\log [S]_0$ gives a straight line with a positive slope of unity indicating that the order with respect to substrate is also one (Table 1).

TABLE 1—EFFECT OF VARYING [SUBSTRATE] ON THE RATE OF REACTION

[Vanadium(V)] = 0.005 M [Glycollic acid] (10^{-2} M)	$[H_2SO_4] = 2$ M, 10^{-4} K (sec^{-1})	temp. = 40° $10^{-2}K_0$
2.00	6.41	32.04
1.42	4.14	29.20
1.25	3.74	29.90
1.11	3.34	30.07
1.00	3.06	30.60

$k_0 = k/[\text{Substrate}]$

The plot of $1/k$ vs $1/[S]_0$ gives a straight line passing through the origin. This may be taken as a kinetic evidence of the fact that no intermediate compound was formed between vanadium(V) and glycollic acid.

Effect of $[H_2SO_4]$ *on the reaction rate:* The rate of reaction was found to increase on increasing $[H_2SO_4]$. At 5 M and above, the reaction was practically instantaneous. The plot of $\log k$ vs $\log [H_2SO_4]$ was linear with an intercept obeying Eq. (1).

$$\log k = 1.2 \log [H_2SO_4] - 3.74 \quad \text{... (1)}$$

Effect of $[H^+]$ *on the reaction rate:* At constant ionic strength and constant [bisulphate], the plot of k vs $[H^+]^2$ was found to be linear passing through the origin (Fig. 1). As no positive intercept was obtained, it may be supposed that the reaction involves only one path with a rate directly proportional to $[H^+]^2$ and the order with respect to $[H^+]$ was found to be two.

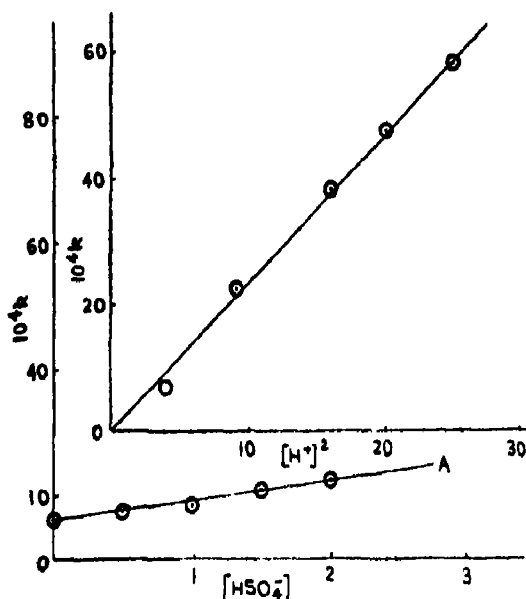
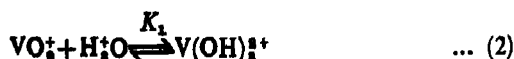


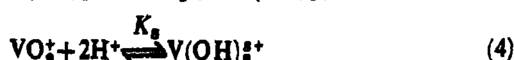
Fig 1. Plot of k vs $[HSO_4^-]$ at $\mu=4$ and plot of k vs $[H^+]^2$ at $\mu=6$.
[Glycollic acid]=0.0125 M [Vanadium(V)]=0.005 M and temp=40°

Effect of $[HSO_4^-]$ *on the reaction rate :* The plot of k vs $[HSO_4^-]$ was found to be linear with a positive intercept (Fig. 1). This suggests no direct dependence of rate on $[HSO_4^-]$.

Reactive species of V(V) : The parent reactive species of V(V) in mineral acid is supposed to be present as VO_2^+ which is converted into different forms depending on $[H_2SO_4]$ according to equilibria (2-5).


$$VO_2^+ + H_3O^+ \overset{K_1}{\rightleftharpoons} V(OH)_3^{2+} \quad \text{... (2)}$$


$$V(OH)_3^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} V(OH)_3(HSO_4)^+ \quad (3)$$


$$VO_2^+ + 2H^+ \overset{K_3}{\rightleftharpoons} V(OH)_2^{3+} \quad (4)$$


$$V(OH)_2^{3+} + HSO_4^- \overset{K_4}{\rightleftharpoons} V(OH)_2(HSO_4)^{2+} \quad (5)$$

The linear dependence of the rate on $[H^+]^2$ rules out equilibria (2) and (3), and leads us to conclude that $V(OH)_2^{3+}$ is the real active oxidising species of V(V) and there is no hydrogen ion independent path involving VO_2^+, as the plot of k vs $[H^+]^2$ passes through the origin. The increase in rate with increase in $[HSO_4^-]$, evident from the linear plot of k vs $[HSO_4^-]$ having a positive intercept, suggests that the species $V(OH)_2(HSO_4^-)^{2+}$ are better oxidant than $V(OH)_2^{3+}$.

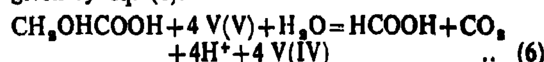
Effect of $[NaClO_4]$ *and* $[MnSO_4]$ *on the reaction rate :* No appreciable change in the rate (Table 2) was obtained on increasing $[NaClO_4]$ which indicates that for all practical purposes change in ionic strength had no effect. This naturally suggests participation of the substrate as a neutral molecule[3] because oxidant is ionic in nature. Increase in $[MnSO_4]$ has a tendency to accelerate the rate of reaction (Table 2). This effect cannot be due to change in the ionic strength of the medium. Mn(IV) has been found to be a good oxidant for the glycollic acid oxidation[5]. It is likely that Mn(IV) obtained from the oxidation of Mn(II) by V(V) is responsible for accelerating the rate of reaction.

TABLE 2—EFFECT OF VARYING $[NaClO_4]$ AND $[MnSO_4]$ ON THE REACTION RATE

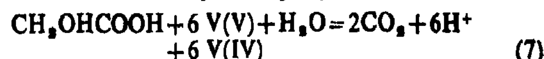
[Glycollic acid]=0.0125 M, [Vanadium(V)]=0.005 M, temp =40°

$[NaClO_4]$ (M)	–	0.05	0.10	0.50	–	–	–
$[MnSO_4]$ (M)	–	–	–	–	0.025	0.050	0.075
$10^{-4}k$ (sec^{-1})	3.71	3.95	3.88	3.61	3.80	4.02	4.09

Stoichiometry : The stoichiometry of the reaction was studied potentiometrically. Below 3.5 M H_2SO_4 acid medium the stoichiometry was calculated to be four moles of vanadium(V) for one mole of glycollic acid. The final product was found to be formic acid which was identified by chromotropic acid tests[4]. The overall equation can be given by Eq. (6).


$$CH_2OHCOOH + 4\,V(V) + H_2O = HCOOH + CO_2 + 4H^+ + 4\,V(IV) \quad \text{.. (6)}$$

Above 3.75 M H_2SO_4 medium the overall reaction was found to satisfy the Eq. (7).


$$CH_2OHCOOH + 6\,V(V) + H_2O = 2CO_2 + 6H^+ + 6\,V(IV) \quad (7)$$

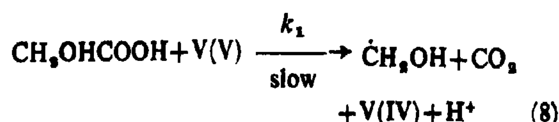
The absence of formaldehyde or formic acid was confirmed by chromotropic acid tests. Only one inflexion, both in direct (substrate in the cell) and reverse (oxidant in the cell) potentiometric titrations, was obtained corresponding to the abovementioned stoichiometries in both the acid ranges used. This leads us to conclude that the expected intermediate oxidation products get oxidised to the final stage in a fast process.

Influence of temperature : Parallel Arrhenius plots were obtained for both the acid ranges used, suggesting the same rate determining steps in either acid range. From Arrhenius plot, the energy of activation, frequency factor and entropy of activation were calculated and found to be 13.68 Kcal mol^{-1}, 10.77×10^7 and -21.84 e. u. respectively.

Mechanism : On the basis of various experimental observations described, it is now possible to suggest a mechanism of oxidation of glycollic acid by V(V) in sulphuric acid medium. V(V) like Cr(VI) can act both as one or two electron oxidant[6]. In the present case it acts as one electron oxidant because the reaction involves free radical intermediate as is evident from acrylonitrile test. Similar observations have been made by Water and Littler during their studies on V(V) oxidation of alcohols,

ketones and other substrates[6]. The reactive species of V(V) namely $V(OH)_3^{2+}$ and $V(OH)_3(HSO_4)^{2+}$ react with glycollic acid to give free radicals in a slow rate-determining ste accompanied by C–C bond fission as it has been suggested by Jones *et al*[7] in the case of oxidation of other α-hydroxy acids by V(V).

In general the reaction can be written as given below.



$$CH_2OHCOOH+V(V) \xrightarrow[\text{slow}]{k_1} \dot{C}H_2OH+CO_2 +V(IV)+H^+ \quad (8)$$

The free radical so formed is readily oxidised to formaldehyde



$$\dot{C}H_2OH+V(V) \xrightarrow[\text{fast}]{} HCHO+H^++V(IV) \quad (9)$$

Further oxidation of HCHO into formic acid and finally to carbon dioxide, depending on acid concentration, also takes place through fast steps. Thus the rate equation (10) may be derived.

$$-\frac{d[V(V)]}{dt}=k_1[S][V(V)]_T \quad \ldots (10)$$

Considering both the active species of V(V) the rate equation may be represented by Eq. (11).

$$-\frac{d[V(V)]}{dt}=K_2k_1[S][VO_2^+][H^+]^2\{1+K_4[HSO_4^-]\} \quad \ldots (11)$$

If bisulphate complex of V(V) is not considere Eq. (11) is reduced to the following form :

$$-\frac{d[V(V)]}{dt}=K_2k_1[S][VO_2^+][H^+]^2 \quad \ldots (1$$

The rate equation so derived is well in conformi with the experimental findings.

Acknowledgement

The award of a teacher fellowship to one of t authors (J. C.) by the U. G. C., New Delhi is grat fully acknowledged.

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Decomposition of Propan-2-ol over Chromite Spinels—Kinetic Studies

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The decomposition of propan-2-ol has been investigated over copper, zinc and cobalt chromite catalysts in the vapour phase in a flow reactor. The decomposition of propan-2-ol to acetone follows a first order kinetics. The kinetic data obtained on zinc oxide are also included to show the better performance of the spinel compared to simple oxide. The order of reactivity for the decomposition shows the following order: cobalt chromite<zinc chromite<copper chromite. Zinc and cobalt chromites are more active when they are pretreated in oxygen than in hydrogen. Over zinc chromite the desorption of acetone is found to be the rate controlling step. However, over cobalt chromite the desorption of hydrogen is what determines the rate

SPINELS are mixed metal oxides represented by general formula AB_2O_4, where A and B represent bivalent (Cu, Co, Ni, Mn, Zn, Mg) and trivalent (Al, Fe, Cr) metals, respectively. Spinels are reported to be thermally stable and they maintain enhanced and sustained activity for a variety of industrially important reactions such as decomposition of nitrous oxide[1], hydrodesulphurization of petroleum crudes[2], oxidation and dehydrogenation of hydrocarbons[3,4] and methanation of carbon monoxide[5]. Considering the decomposition of propan-2-ol, Kuriacose *et al*[6,7] have investigated this reaction over Zn : Cr . Fe and Cr_2O_3 catalysts. Copper catalyst has been used by Gryazova *et al*[8] for the dehydrogenation, while silver catalyst has been employed by Stadnik[9] for the oxidation, of propan-2-ol. Some of the other catalysts used for this reaction were indium oxide[10], η-Al_2O_3, θ-Al_2O_3, $MgAl_2O_4$[11] and alkali cation exchanged zeolites[12]. In the present investigation, $CuCr_2O_4$, $ZnCr_2O_4$, $CoCr_2O_4$ and ZnO have been prepared and their catalytic activities in the kinetic decomposition of propan-2-ol to acetone have been compared, which have not so far been reported.

Experimental

Preparation of materials : The catalysts were prepared by the following methods[13]. The nitrates of the metals employed for the preparation of the catalysts were AnalaR (B.D.H.) samples and used as such. 10% solutions of the nitrates in water were prepared and they were mixed in the molar ratio M (M=Co, Zn, Cu) : Cr=1 2 and the mixture was heated to 60-80°. To the hot mixture, a 5% ammonia solution was added dropwise with constant and uniform stirring. In the case of cobalt chromite the *p*H of the solution was maintained at 8 and in other cases it was kept at 6.5 during the precipitation. The mixture was digested for another 2 hr at the same temperature to complete precipitation. The precipitate was filtered and dried in an air oven at 80° for 24 hr. Calcination of copper and cobalt chromites was done at 650°, while of zinc chromite at 700° for 8 hr, in an atmosphere of circulating air. Formation of spinels was checked by X-ray diffraction[13,14].

Propan-2-ol AnalaR (B.D.H.) was distilled before use and its purity was more than 99% by gas chromatographic analysis.

Apparatus and procedure · The reactions were carried out at atmospheric pressure in a fixed bed flow type reactor using 20-40 mesh size catalyst. The experimental procedures were the same as described earlier[15].

Orsat's gas analyser was used for analysing the gaseous products. The liquid products were identified and estimated by an AIMIL dual column gas chromatograph, using an one meter column of carbowax on chromosorb.

On all the four catalysts, acetone was the main product. In addition to acetone, a small amount of 4-methyl-2-pentanone (MIBK) was obtained on copper chromite. The gaseous products consisted mainly of hydrogen with traces of propene and carbon dioxide.

Results and Discussion

From the effect of contact time, W/F (where W is weight of catalyst and F is flow rate), on the overall conversion of propan-2-ol the values of log(1/1-x) were evaluated and plotted against contact time in Fig. 1. The straight line plots indicate that the decomposition of propan-2-ol to acetone follows first order kinetics. The rate constants calculated from the slopes (slope=k/2.303) of these plots are presented in Table 1 which are also compared with the rate constants obtained from the first order equation.

The formation of acetone as a function of contact time over $CuCr_2O_4$, $ZnCr_2O_4$ and $CoCr_2O_4$

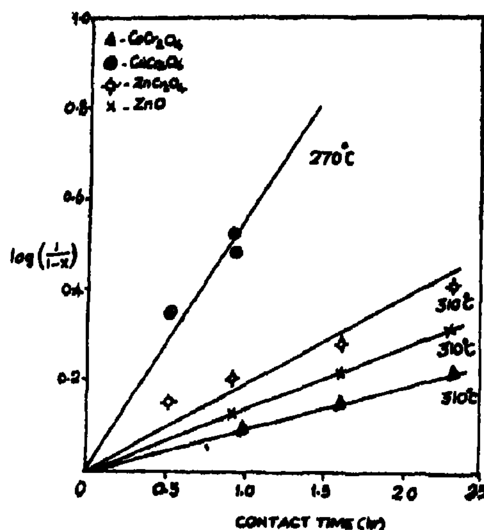


Fig. 1. First order plots.

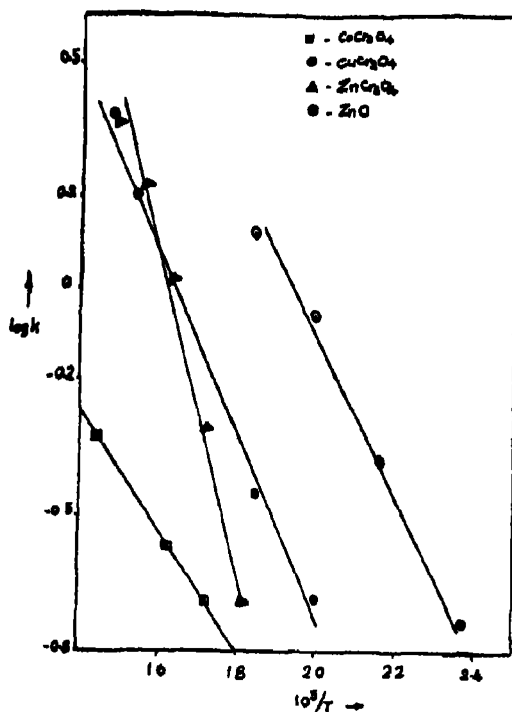


Fig. 1a Arrhenius plots

are plotted in Figs. 2-4, respectively. The rate of formation of acetone is higher at the beginning as could be seen from slopes of these curves. At higher contact time, a part of the adsorbed acetone may be oxidised to CO_2 by the lattice oxygen. This is evident from the evolution of CO_2 during the reaction. The mole percentage of CO_2 obtained for $CuCr_2O_4$ at contact times of 0.5, 0.9 and 1.6 hr are 1.3, 3.7 and 6.4, respectively. Evolution of CO_2 over other catalysts were negligible. The formation of CO_2 has been further confirmed by carrying

TABLE 1—RATE CONSTANTS FROM THE SLOPES OF THE FIRST ORDER PLOTS AND FROM THE FIRST ORDER EQUATION

Temp. °C	Rate constant k (hr^{-1}) from the first order equation: ZnO	$ZnCr_2O_4$	$CoCr_2O_4$	$CuCr_2O_4$
150				0.7488
185	0.0458			
190				0.3804
230	0.2070			0.8708
270	0.6498			1.3020
280		0.2083		
310	0.3050	0.4875	0.2085	
340	0.7055	1.0450		
345			0.2668	
370	1.6880	1.6990		
400	2.4580	2.3200		
420			0.3169	
From the slope	0.3070 (310°)	0.4880 (310°)	0.2860 (310°)	1.2500 (270°)

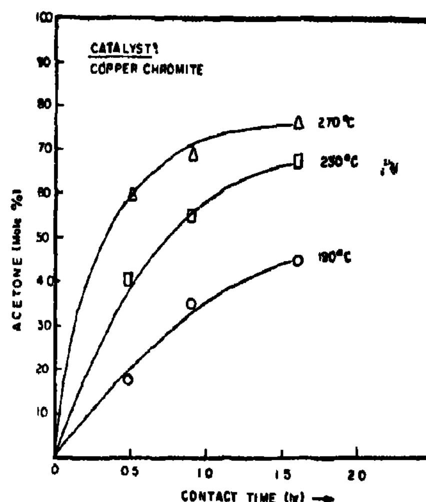


Fig 2. Effect of contact time on the formation of acetone over $CuCr_2O_4$.

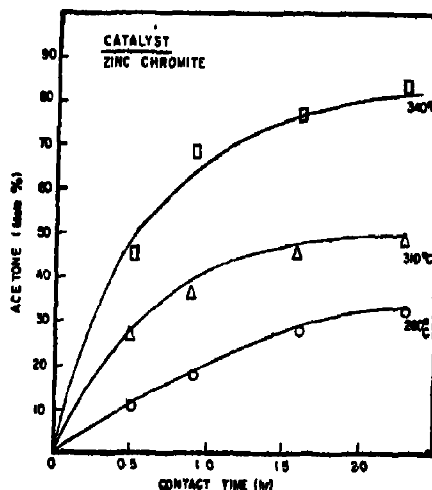


Fig. 3. Effect of contact time on the formation of acetone over $ZnCr_2O_4$.

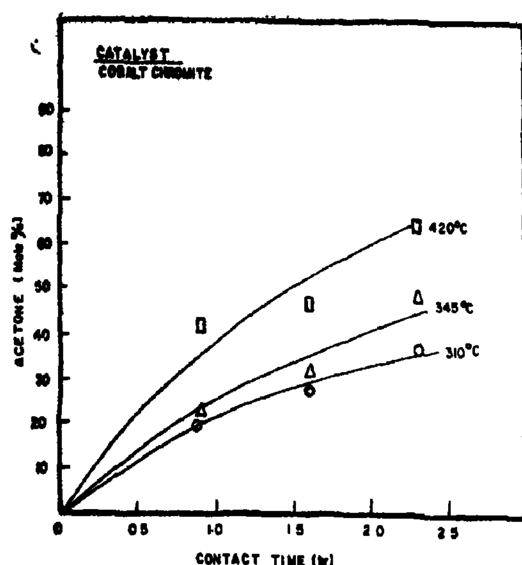


Fig 4 Effect of contact time on the formation of acetone over $CoCr_2O_4$

out runs with acetone alone over $CuCr_2O_4$. A second factor for lower rate of formation of acetone at higher contact time may be due to the reverse reaction as reported by Kuriacose *et al*[16].

Zinc and cobalt chromites, when pretreated in an atmosphere of hydrogen, showed a decrease in catalytic activity for the decomposition of propan-2-ol (Table 2). On chromite spinels the Cr(III)

TABLE 2—EFFECT OF PRETREATMENT
CONTACT TIME 0.9 hr

Catalyst	Temp °C	Pretreatment	Acetone (mole%)
Zinc chromite	310	oxidised	37
	310	reduced	25
	340	oxidised	68
	370	oxidised	81
	370	reduced	62
Cobalt chromite	310	oxidised	20
	310	reduced	17
	345	oxidised	33
	380	oxidised	56
	380	reduced	39

ions could be the active sites for the dehydrogenation. This view was confirmed in solid solutions of nickel-aluminium-chromium oxide[17]. When the catalyst is kept in an atmosphere of hydrogen the Cr(III) ions may probably be reduced to Cr(II) ions. Chromous ions may be less effective for the dehydrogenation of alcohols, though they were reported to be active in the dehydrogenation of hydrocarbons[18]. In addition, hydrogen may strip off several layers of lattice oxygen during reduction, which involve in the oxidative dehydrogenation of propan-2-ol. The occurrence of oxidative dehydrogenation in addition to the normal dehydrogenation has been confirmed by working out the material balance between the amount of acetone formed and the volume of hydrogen evolved.

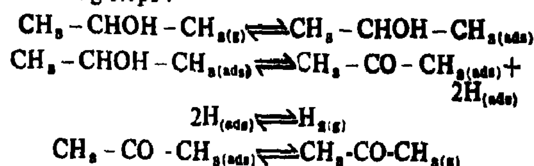


$$>CHOH+(O)_{lattice} \longrightarrow CO_2+H_2O$$

The activation energies in k. J/mole for the catalysts $CoCr_2O_4$, $ZnCr_2O_4$, $CuCr_2O_4$ and ZnO are 25.75, 67.63, 34.28 and 51.37, respectively. For the decomposition of propan-2-ol, $CuCr_2O_4$ exhibits maximum activity followed by $ZnCr_2O_4$ and $CoCr_2O_4$, respectively. $CoCr_2O_4$ has the lowest activation energy and hence it may be expected to show the maximum activity. But it is found to be the least active, probably due to different active sites that are involved in the decomposition reaction.

Comparing the activity of $ZnCr_2O_4$ with ZnO, the latter is found less active than the former. This proves that a spinel is a better catalyst than a simple oxide.

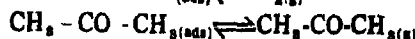
Product inhibition studies were carried out with an assumption that the main reaction viz. the dehydrogenation of propan-2-ol proceeds by the following steps:



$$CH_3-CHOH-CH_{3(g)} \rightleftharpoons CH_3-CHOH-CH_{3(ads)}$$

$$CH_3-CHOH-CH_{3(ads)} \rightleftharpoons CH_3-CO-CH_{3(ads)}+2H_{(ads)}$$

$$2H_{(ads)} \rightleftharpoons H_{2(g)}$$



$$CH_3-CO-CH_{3(ads)} \rightleftharpoons CH_3\text{-}CO\text{-}CH_{3(g)}$$

The rate of dehydrogenation is not affected by diluent hydrogen over $ZnCr_2O_4$ (Table 3). This

TABLE 3—PRODUCT INHIBITION ON THE % FORMATION OF ACETONE OVER ZINC CHROMITE AND COBALT CHROMITE CONTACT TIME 0.9 hr.

Catalyst	Temp °C	Oxidised		Reduced	
		No diluent	Diluent acetone (5 mole %)	No diluent	Diluent H_2 (9.5 ml/min)
$ZnCr_2O_4$	310	37	23	25	23
	340	68	45	44	42
	370	81	69	62	59
$CoCr_2O_4$	310	20	19	17	11
	345	33	31	24	15
	380	56	55	39	27

indicates that the desorption of hydrogen is much faster. Teichner[19] and coworker have arrived at the same conclusion for ZnO. However, diluent acetone considerably retards the rate of dehydrogenation. The rate of desorption of acetone must be slower and it may be the rate controlling step.

On $CoCr_2O_4$, acetone has negligible effect on the rate of reaction but hydrogen affects the reaction to a considerable extent (Table 3) and it is the desorption of hydrogen that may control the rate of the reaction.

Conclusion :

All the four catalysts used are highly selective in dehydrogenating propan-2-ol to acetone. Their dehydration ability is meagre. Copper chromite is the most effective catalyst even in the low temperature regions.

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Gas-liquid Chromatographic Study of Molar Heats of Evaporation : Effect of Molecular Structure

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Gas-liquid chromatography, using a short copper column (2 meters long) with adequate liquid phase coating (Silicone Elastomer SE-30) provides typical conditions for separation, identification and calculation of some thermodynamic constants of various highly divergent organic compounds, including high-boiling *normal* alkylated benzenes, halogenated aromatic rings and chlorinated hydrocarbons. The technique also provides a means to trace the effect of molecular structure upon thermodynamic values like molar heats of evaporation. Especially important is the role of inter- and intramolecular hydrogen bondings such as molecular orientation in space and polarisabilities of molecules in specific circumstances.

GAS-liquid chromatography technique is used for the determination of molar heats of evaporation (ΔH) of some alkylbenzenes, halogenated benzenes, alcohols and chlorinated hydrocarbons on silicone elastomer SE-30 as the liquid phase (coating solvent). Most data are new and provide good information about different factors affecting the solution and evaporation of these solutes on specific surfaces other than the known effect on the boiling point of each solute.

Experimental

(a) *Setup :* A PYE Unicam GLC (Pye Series 104 Chromatograph) is used. It is equipped with a flame-ionization detector and a PM 8220 recorder.

(b) *Columns :* A copper column, (length 2 meter, i.d. 5 mm) is used. It is packed with SE-30 (15% w/w) liquid phase on Diatomite (solid support, 60-70 mesh).

(c) *Chemicals :* Aldrich and B D.H. chemicals were used. Purity of chemicals was tested chromatographically. Each chemical gave only one peak, applying the highest recorder sensitivity.

(d) *Working parameters :*

Detector temp.	= 240°.
Hydrogen pressure	= 12.5 lb/in².
Air pressure	= 5 lb/in².
Flow rate	= 30 ml/min.
Recorder speed	= 0.5 cm/min.
Gas carrier	= Nitrogen.

These parameters were kept constant for all the experiments.

(e) *Samples :* Four systems were investigated

1. *n*-Alkylbenzenes
2. Halogenated benzenes
3. *n*-Alcohols
4. Chlorinated hydrocarbons

Chemicals composing each system were injected with the aid of a micro syringe. Sample volume was 0.15 μl. Injections of individual compounds were also made prior to every collective run to ensure a complete resolution of peaks. No overlap between peaks was observed because of the careful selection of temperature ranges.

Calculations of ΔH : In order to calculate the molar heat of evaporation (ΔH) of each compound the retention time t_R is multiplied by the flow rate to get the retention volume V_R. This retention volume is then corrected to zero degree and per gram solvent (liquid phase) to yield the specific retention volume V_g

$$V_g = \frac{V_R \times 273}{W_L \times K}$$

where W_L is the weight of silicone elastomer in gram[1] and K is the absolute temperature of the column.

Plots of log V_g against $10^3/K$ yielded straight line. According to the equation $\log V_g = \frac{\Delta H}{2.3\,RT} + k$, initially proposed by Littlewood *et al*[2] and subsequently modified by Ambrose[1], ΔH should be equal to the slope of such a plot times 2.3R (R = gas constant = 1.987 cal mole^{-1} and k is a constant, characteristic of such an equation). In this way molar heats of evaporation of the systems were calculated. Since ΔH is constant, dependence of log V_g on $10^3/K$ should be linear according to this equation. Present results confirm this fact (Figs. 2, 4, 5).

Results and Discussion

System 1 : The normal *alkylbenzenes :* Six *normal* alkylbenzenes, toluene, *n*-ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *n*-amylbenzene and 1-phenylhexane were studied. The chosen range of

temperatures (100-130°) produced resolutions with excellent peaks (Fig. 1) inspite of the short length of the separation column (2 meters only). Separation and identification of the heavier compounds like *n*-amylbenzene and 1-phenylhexane are of major importance both in petrochemical industries and research studies. 1-Phenylhexane is a principal constituent in diesel fuel. This compound and similar alkylbenzenes have been used as good models for investigating the intramolecular excitation energy transfer[9] in nuclear and radiation chemistry. Owing to its relatively high boiling point (226°) and low volatility, there were some difficulties in the elution of 1-phenylhexane in gas-liquid chromatography.

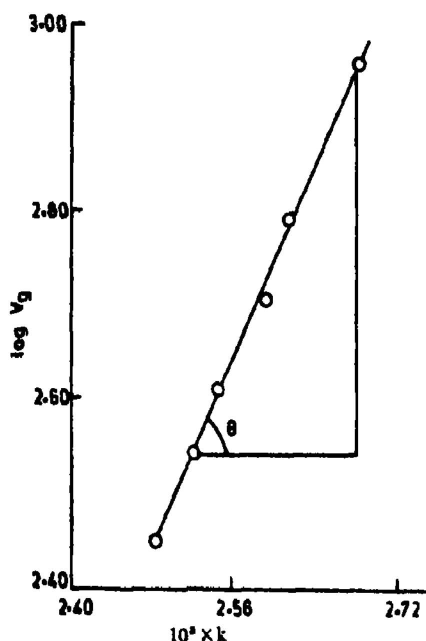


Fig. 1. Dependence of log V_g on temperature
1-Phenylhexane

$$\log V_g = \frac{\Delta H}{2.8\ RT} + k$$

ΔH = Slope × 2.3R

ΔH = 11.600 K cal/mole

Retention time t_R, retention volume V_R, specific retention volume V_g, and log V_g for compounds in system 1 against varying temperature are listed in Table 1. These values decrease with increasing temperature. Retention time at the same temperature increases from toluene to 1-phenylhexane, that is with increasing number of carbon atoms (which evidently results in increasing molecular weights and increasing boiling points) (Table 2).

Molar heats of evaporation: Molar heats of evaporation, ΔH, of the six alkylbenzenes were calculated from slopes of plots similar to those given in Fig. 2. Dependence of log V_g on the reciprocal of the absolute temperature is linear since

TABLE 1

Temp. K	1/K	t_R	V_R	V_g	log V_g
n-Propylbenzene : (ΔH = 7.4198 K cal/mole)					
378	2.68×10^{-3}	11.2	336	146.38	2.165
383	2.61×10^{-3}	9	270	114.55	2.059
388	$2\ 57 \times 10^{-3}$	7.8	234	98.002	1.991
393	2.54×10^{-3}	7	210	86.882	1.938
398	$2\ 51 \times 10^{-3}$	6 4	192	78 391	1 894
403	$2\ 48 \times 10^{-3}$	5 4	162	65 322	1.815
n-Ethylbenzene (ΔH = 7.337 K cal/mole)					
		7.2	216	94 101	1.973
		5.8	174	73 825	1 868
		5.0	150	62.822	1.798
		4.6	138	57.061	1 756
		4.4	132	53 894	1 731
		3 4	102	41.129	1 614
Tolnene : (ΔH = 5.474 K cal/mole)					
		4	120	52 278	1 718
		3.8	114	48.36	1.684
		3.2	96	40.206	1.604
		3	90	37.218	1.570
		3	90	36.746	1 565
		2.2	66	26.610	1.425
1-Phenylhexane (ΔH = 11.500 K cal/mole)					
		69	2070	. 901.809	2 955
		48 8	1464	621 14	2.793
		41	1230	515.141	2 711
		34	1020	421 755	2 625
		29.2	876	357.666	2 553
		24	720	290 322	2 462
Amylbenzene (ΔH = 10 2442 K cal/mole)					
		37 4	1122	488.806	2.689
		27	810	343.666	2 536
		23 6	708	296.52	2.472
		20	600	243 75	2.3874
		17 2	516	210 678	2.323
		14 4	432	174.198	2.241
n-Butylbenzene . (ΔH = 9.0068 K cal/mole)					
		21	630	274.463	2.438
		15 8	474	201 106	2 303
		13 4	402	168.363	2.226
		12	360	148.854	2 172
		10 4	312	127.386	2.105
		8.8	264	106.451	2.027

TABLE 2

System 1 : Alkylbenzenes
Temperature = 378 K

Compound	M W.	b.p. °C	t_R	V_R	V_g	log V_g
Toluene	92	110	4	120	52.278	1.718
n-Ethylbenzene	106	136	7.2	216	94 101	1.973
n-Propylbenzene	120	159	11 2	336	146 30	2.165
n-Butylbenzene	134	183	21	680	274.468	2.438
n-Amylbenzene	148	204	37 4	1122	486.806	2.689
n-Phenylhexane	162	226	69	2070	901.809	2.955

the molar heat of evaporation is constant. Deviation from linearity reflects a variation in density of the compound under investigation with temperature. This was observed in the case of toluene (b.p. = 110°) where 4 out of 6 experiments were done at temperatures higher than its boiling point and considerable fluctuations were observed (Table 1). Lowering temperature ranges deteriorated the whole situation where heavier members did not elute at all.

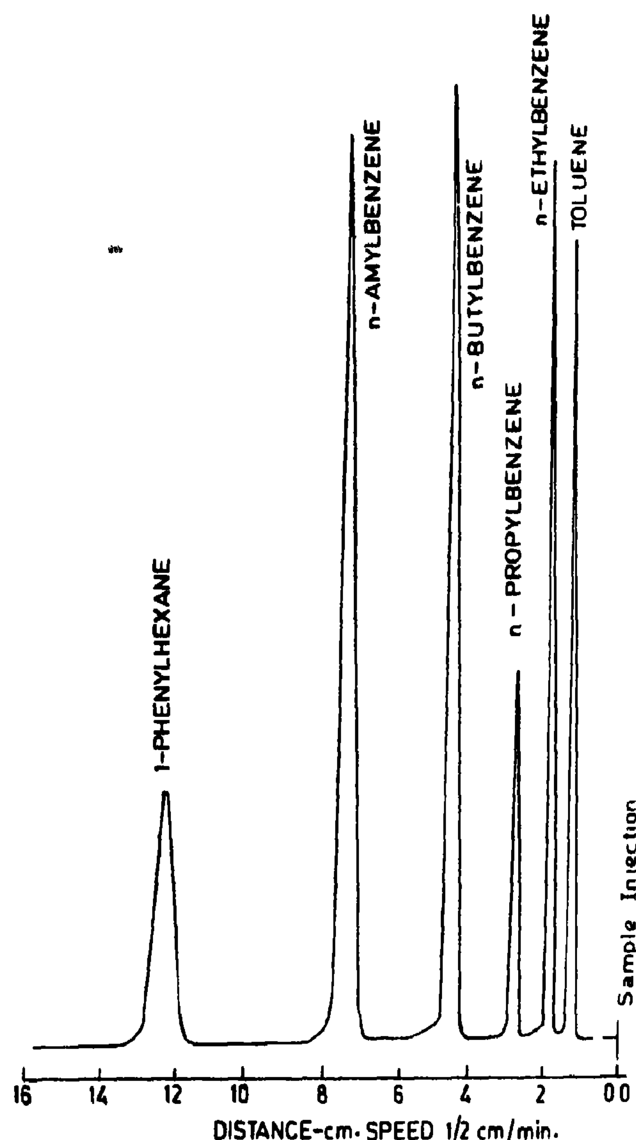


Fig 2 Chromatogram of a mixture of n-alkylbenzenes. Separation from column containing 15% SE-30 on Diatomite. System 1 . Alkylbenzenes column temp. . 130°, Flow rate = 80 ml/min

Molar heats of evaporations for system 1 are listed in Table 3 and plotted in Fig. 3 against the number of carbon atoms in the side chain (the alkyl group). They show linear dependence. The explanation for this lies in the structure of these successive *normal* alkylbenzenes. There is a constant difference of 14 units of mass (mass of CH_2 group) between any two successive compounds. The corresponding boiling points also have almost constant difference (21-25°) (see Table 3).

System 2 : Halogenated benzenes : Four compounds viz. fluoro-, chloro-, bromo- and iodobenzenes were studied to investigate the effect of the different halogen atoms, attached to the benzene ring upon molar heat of evaporation of these compounds.

In cases of these compounds also, the values of t_R and log V_g decrease with increasing temperature (Table 4). Further, t_R and log V_g as well as molar heats of evaporation increase with increasing molecular weight (and resultant increase in boiling points) of these compounds (Table 5). It is also found that the differences in values of ΔH are solely attributable to the differences in masses of the attached halogen atoms (Table 6).

TABLE 3

System 1 Alkylbenzenes

Compound	M.W	b.p °C	No of carbon atoms in the side chain	ΔH K cal/mole
Toluene	92	110	1	5.474
n-Ethylbenzene	106	135	2	7.387
n-Propylbenzene	120	159	3	7.4198
n-Butylbenzene	134	183	4	9.0068
n-Amylbenzene	148	204	5	10.2442
1-Phenylhexane	162	226	6	11.500

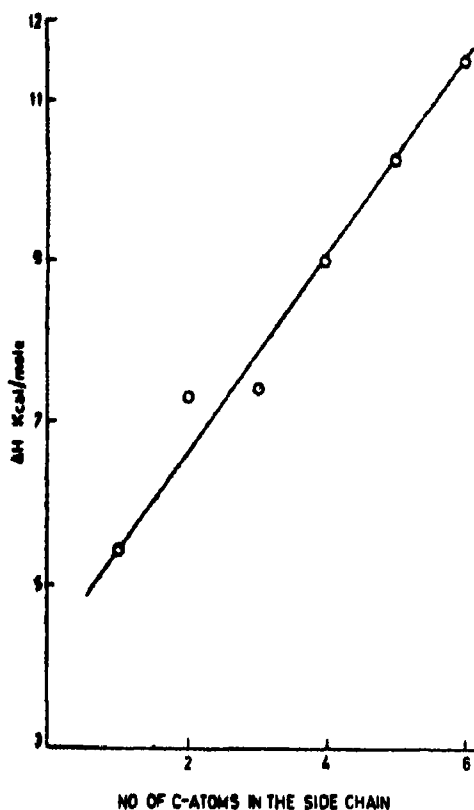


Fig 3

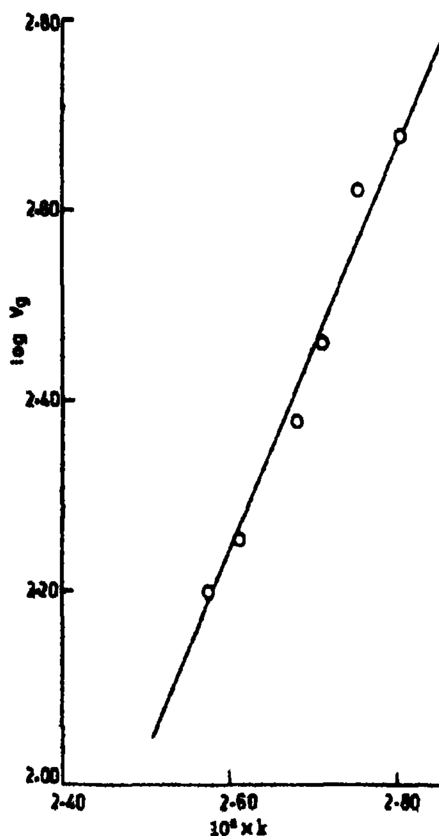


Fig. 4. Iodobenzene.

TABLE 4

System 2 : Halogenated Benzenes

Compound	Temp. (K)	358	363	368	373	383	388
Fluorobenzene	t_R	4	4	3	2.8	2.6	2.6
	$\log V_g$	1.7361	1.7301	1.599	1.563	1.519	1.5141
Chlorobenzene	t_R	11	10	7.4	6.6	5.6	5.1
	$\log V_g$	2.1754	2.128	1.991	1.935	1.852	1.8067
Bromobenzene	t_R	18.5	16.8	12	10.3	8.3	7.6
	$\log V_g$	2.4012	2 358	2.201	2.129	2.038	1.9799
Iodobenzene	t_R	35	31 6	22	18.5	14.2	12.6
	$\log V_g$	2.6781	2.627	2.464	2.388	2.257	2.1945

TABLE 5

System 2 . Halogenated Benzenes

Temperature = 373 K

Compound	M.W	b.p °C	t_R	V_R	V_g	$\log V_g$
Fluorobenzene	96	85	2 8	84	36 594	1 563
Chlorobenzene	112.5	132	6.6	198	86.258	1 935
Bromobenzene	157	156	10.3	309	134 615	2.129
Iodobenzene	204	188	18 5	555	241.785	2.3834

TABLE 6

System 2 Halogenated Benzenes

Compound	Mass of the attached halogen atom	ΔH, K cal/mole
Fluorobenzene	19	5 428
Chlorobenzene	35 5	8 625
Bromobenzene	80	9 20
Iodobenzene	127	10 0556

The difference in the values of molar heat of evaporation of fluorobenzene and chlorobenzene is too large, compared to the difference in ΔH values of chlorobenzene and bromobenzene or of bromobenzene and iodobenzene. Halogenated benzenes (other than the fluoro- one) have in general low boiling points but they have relatively high molar heats of evaporation as we shall see later (Table 12). All of them display small peaks compared to the peaks of other compounds. This might be the consequence of bad combustion in hydrogen. Especially important is the nature of the halogen atom attached to benzene ring. We should therefore find the explanation in the combination of a halogen atom with a single aromatic ring and the probable mutual interaction of the six π electrons in the benzene ring with the strongest electronegative atoms having the highest electron affinities among other elements in the periodic table. Fluorine, however, has its own peculiarities[4,5].

A comparison between system 1 and system 2 is shown in Table 7. Both of them have the aromatic ring of benzene. Fluorobenzene is an exception, having larger molecular weight and smaller boiling point than toluene.

It is interesting to note that ΔH values of chloro- and bromobenzenes are higher than ΔH values of *n*-ethyl- and *n*-propylbenzenes although the former compounds have lower boiling points (but higher molecular weights) than the latter.

More interesting is the comparison of bromobenzene with *n*-butylbenzene, where the first has a slightly larger ΔH value but a considerably smaller boiling point than the second. If it is a matter of difference in molecular weights, GLC will have to have a new outlook to explain such findings and to answer the question of how does a more volatile compound (bromobenzene) have a higher molar heat of evaporation than a less volatile compound having less ΔH value. Differences in types of interactions of solutes with the same liquid phase are able to answer such a question. If this particular column is replaced by another one having a different packing with different liquid phase, the whole picture may be reversed.

TABLE 7—COMPARISON BETWEEN VALUES OF ΔH FOR THE COMPOUNDS SYSTEMS 1 AND 2. ALL COMPOUNDS HAVE THE AROMATIC RING OF BENZENE

Compound	M.W	b.p °C	ΔH, K cal/mole
Toluene	92	110	5.474
n-Ethylbenzene	106	135	7.337
n-Propylbenzene	120	159	7.4198
n-Butylbenzene	134	183	9.0068
Fluorobenzene	96	85	5.428
Chlorobenzene	112.5	132	8.625
Bromobenzene	157	156	9.200
Iodobenzene	204	188	10.0556

System 3 · n-alcohols : The intermolecular hydrogen bonding effect : Four normal alcohols viz., amyl alcohol, hexanol, heptanol and octanol, were studied to examine the effect of the intermolecular hydrogen bonds on retention times of these alcohols and their molar heats of evaporation. The higher alcohols were chosen because there is no previous studies on the calculations of their molar heats of evaporation. Values of t_R and log V_g at five different temperatures are shown in Table 8. These values decrease with increasing temperature but increase with increasing molecular weights down the group. Fig. 5 illustrates the inverse dependence of log V_g for *n*-octanol on temperature. It increases with decreasing temperature. Dependence, as it is expected to be, is linear as a result of the constancy of ΔH.

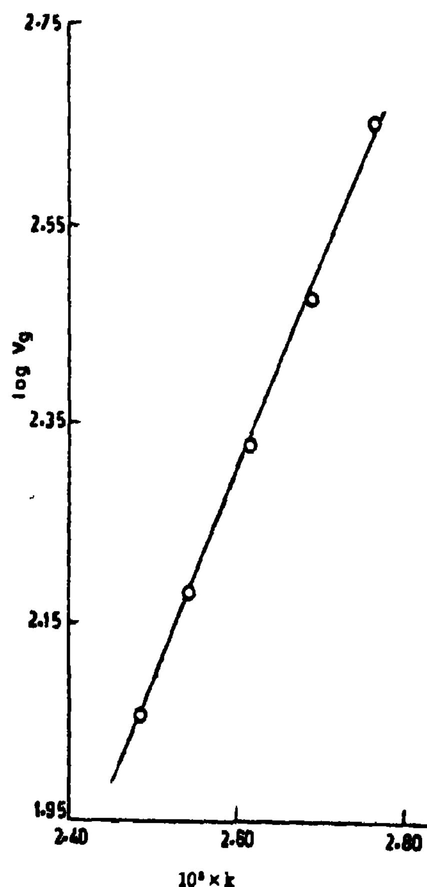


Fig. 5 Octanol.

TABLE 8

System 3 : *n*-Alcohols

Compound	Temp. K	363	373	383	395	403
	10^3/K	2.754	2.680	2.610	2.544	2.481
Amyl alcohol	t_R	4.4	3.6	3.0	2.4	2.4
	log V_g	1.771	1.6725	1.5818	1.4787	1.4628
Hexanol	t_R	9.4	7.2	5.8	4.4	4.0
	log V_g	2.101	1.9735	1.8682	1.7870	1.6847
Heptanol	t_R	17.6	13.0	9.6	7.2	6.0
	log V_g	2.373	2.2302	2.0870	1.9509	1.8608
Octanol	t_R	34	23.2	16.8	12.2	9.4
	log V_g	2.659	2.4817	2.3300	2.1799	2.0557

Compared to the members of system 2, these four alcohols have, in general, low molecular weights and high boiling points (Table 9). Differences between the values of ΔH are not regular. They do not reflect the successive increase in methylene group (CH_2) in the alcohols. However, the differences in any two successive boiling points are also almost constant (18-20°).

TABLE 9

System 3 . *n*-Alcohols

Compound	M.W	b.p. At °C	Difference	No. of CH_2 groups	ΔH, K cal per mole
Amyl alcohol	88	138		4	6.7758
			18		
Hexanol	102	156		5	7.6636
			20		
Heptanol	116	176		6	9.946
			18		
Octanol	130	194		7	9.8036

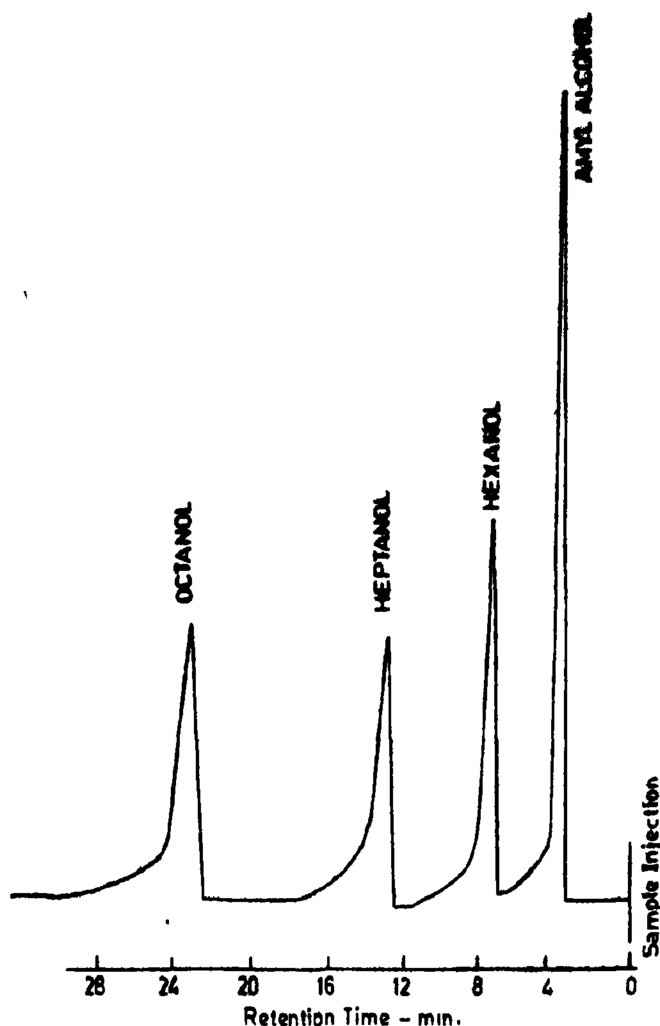


Fig. 6. Chromatogram of a mixture of *n*-amyl alcohol, *n*-hexanol, *n*-heptanol and *n*-octanol.
Column temp. 100°, Flow rate . 80 ml/min, Carrier gas Nitrogen, separation from a column (2 meter long) containing 15% SE-30 on Diatomite.

High boiling points of these alcohols are in fact attributed to the effect of hydrogen bonds existing between hydrogen atoms and oxygen atoms of the hydroxyl group of the neighbouring alcohol molecules. Hydrogen bondings yield intermolecular associations. These associations lower vapour pressure and consequently the volatility.

These associations and the high boiling points are not positively reflected on ΔH values (Table 9) as these values are in fact smaller than those of the four halogenated benzenes (Tables 6 and 7), excluding amyl alcohol which has a higher ΔH value than fluorobenzene.

Shapes of normal alcohols peaks : These four alcohols (especially the higher ones) have eluted with tails (Fig. 6). Raising the column temperature minimises such tails (Fig. 7). The higher the temperature the more symmetrical is the peak. There are several ways in dealing with this problem of tailing. Best results were obtained by introducing the so-called "Tailing Reducer"[1,6] 1.5% squalane deposited on adsorbent (Pelletex).

System 4 : Chlorinated hydrocarbons : Dichloromethane, chloroform and carbon tetrachloride were studied (Tables 10 and 11). Boiling points and molar heats of evaporation increase with increasing number of attached chlorine atoms. Members of this system have in general low boiling points and the lowest molar heats of evaporation.

Like system 2, peaks of these three compounds are very small though they are symmetrical and sharp. Whether this is due to bad combustion in hydrogen or because of an interaction between chlorine atoms and the silicone coating remains to be clarified.

Flame ionization detector has been shown not to be affected by water or carbon dioxide. This

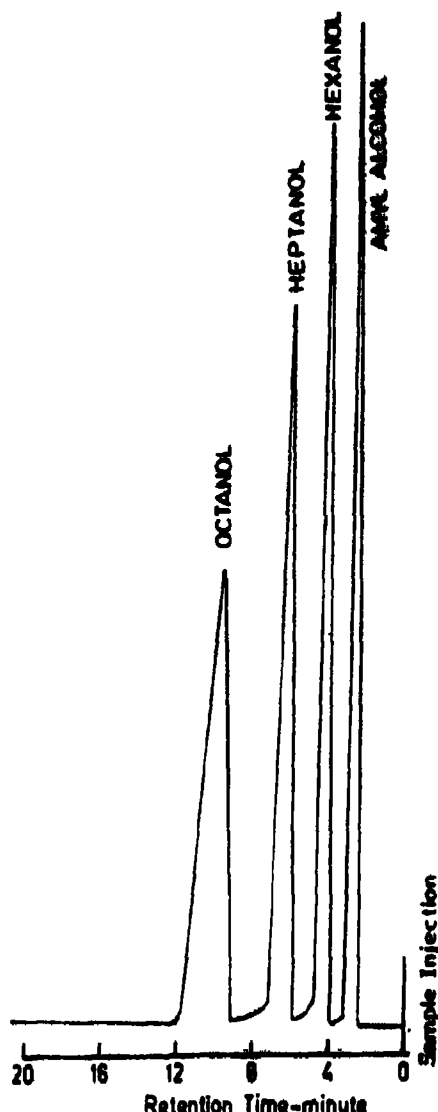


Fig. 7 Chromatogram of a mixture of n-amyl alcohol, n-hexanol, n-heptanol and n-octanol.

Column temp. 130°, Flow rate 30 ml/min, Carrier gas : Nitrogen, separation from a column (2 meter long) containing 15% SE-30 on Diatomite.

TABLE 10

System 4 : CH_2Cl_2, $CHCl_3$, CCl_4

Compound								
	Temp. K	313	323	333	343	348	353	358
	$10^3/K$	3.19	3.096	3.003	2.915	2.873	2.832	2.793
CH_2Cl_2	t_R	2.6	2.6	2.2	1.8	1.8	2.0	1.8
	log V_g	1.6895	1.6259	1.5079	1.4070	1.401	1.4418	1.3693
$CHCl_3$	t_R	4.6	4.6	3.6	3.0	2.8	3.0	2.6
	log V_g	1.8551	1.8415	1.7218	1.6298	1.5935	1.6178	1.5490
CCl_4	t_R	7.0	6.7	5.4	4.4	4.0	4.0	3.4
	log V_g	2.0375	2.0048	1.8979	1.7961	1.7484	1.7422	1.6655

also raises the question of the effect of one, two or three chlorine atoms upon its sensitivity.

TABLE 11

System 4 : CH_2Cl_2, $CHCl_3$, CCl_4

Compound	M. W.	b. p. °C	ΔH, K cal/mole
CH_2Cl_2	85	40	3.46
$CHCl_3$	110	61	3.79
CCl_4	154	77	5.198

It is equally probable that the large reduction in peak size is due to surface adsorption of a major part of the sample itself by inner walls of the copper column[6].

Conclusions and general remarks

Molar heats of evaporation for seventeen compounds were experimentally calculated using GLC technique. Of them, toluene was studies earlier[2,7]. The following table shows different ΔH values of toluene found by different authors using different liquid phases :

	Liquid phase	ΔH, K cal/mole
Present result	SE-30	5.474
Reference 2	Silicone 702	7.9
Reference 2	Tritolylphosphate	9.0
Reference 7	Diisodecylphthalate	8.13

It is evident from this table that different liquid phases yield different ΔH values for the same compound. Smallest ΔH values of toluene correspond to the best surfaces and the easiest means for evaporation. Once evaporation as an endothermic process takes place on such surfaces by the absorption of minimum energy, such surfaces (liquid phases) should be favoured from the economic standpoint.

Silicone Elastomer-30 has proved to be an excellent coating liquid phase. Wide range chemicals of different structures were surprisingly separated and identified. Just one failure is observed. Our column was not able to resolve *m*-xylene from *p*-xylene although it did resolve the *ortho* from the *meta* and *para* isomers (Fig. 8). Lowering oven temperature did not help since *m*- and *p*-xylenes have almost the same boiling points (139 and 138° respectively).

Further experiments have shown that other isomers like *o*- and *m*-chloroanilines are separable on our column at all five temperatures chosen for this experiment.

Contrary to the case of *o*- and *m*-xylenes, the *ortho*-chloroaniline isomer eluted before the *meta* one (Fig. 9). The intramolecular hydrogen bonding existing between chlorine atom and one hydrogen atom in NH_2 group of the same molecule reduces the vapour pressure of *o*-chloroaniline to a lower extent than does the intermolecular hydrogen

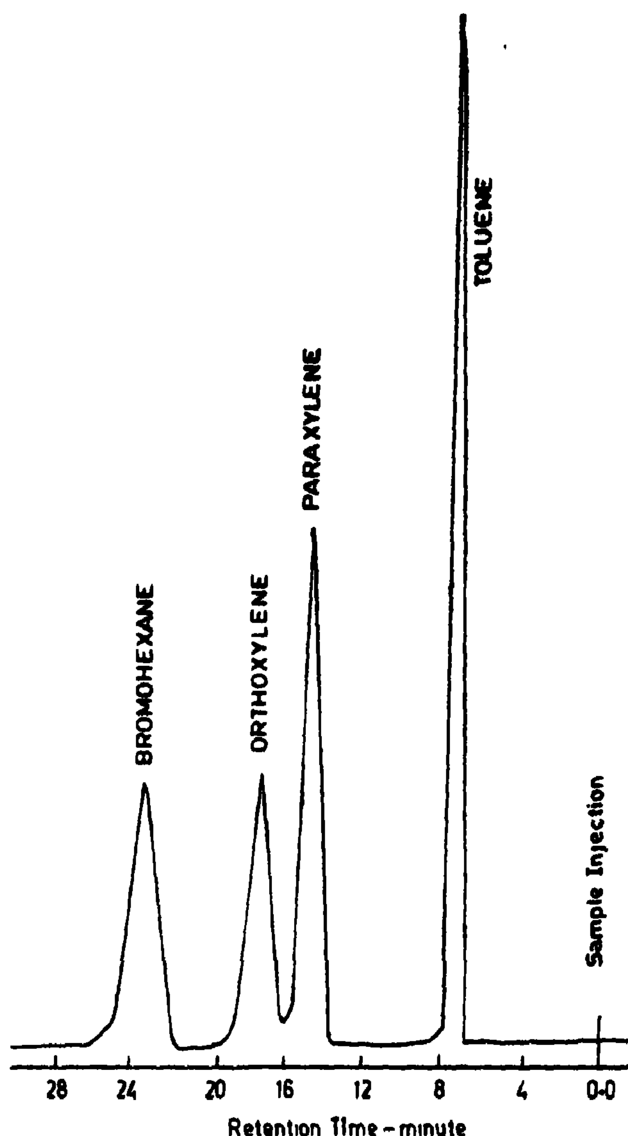
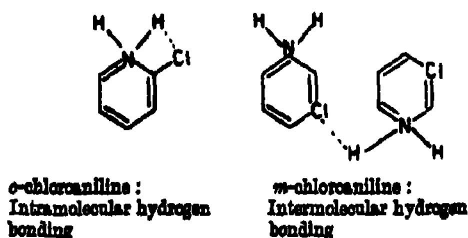


Fig. 8. Chromatogram of a mixture of toluene, p-xylene, o-xylene and bromohexane.
Column temp 70°, Flow rate · 30 ml/min, separation from a column (2 meter long) containing 15% SE-30 on Diatomite.

bonding existing between chlorine atom of one molecule and one hydrogen atom in NH_2 group of a second molecule, giving rise to a fairly well-linked association.



Chloro-, bromo- and iodobenzenes, specially the first two, have in general high molar heats of evaporation with respect to their comparatively low boiling points (Table 12). Contrary to these, normal alcohols have high boiling points but low molecular weights. It seems that the retention of

Table 12—Molar Heats of Evaporation of Some Organic Compounds with Different Structures on SE-30[1] (15% W/W). Numerical Values are Tabulated in an Increasing Order

Compound	M.W.	b. p. °C	ΔH, K cal/mole
CH_2Cl_2	85	40	8.45
$CHCl_3$	119	61	8.79
CCl_4	154	77	5.1980
Fluorobenzene	96	85	5.426
Toluene	92	110	5.474
Amyl alcohol	88	138	6.7758

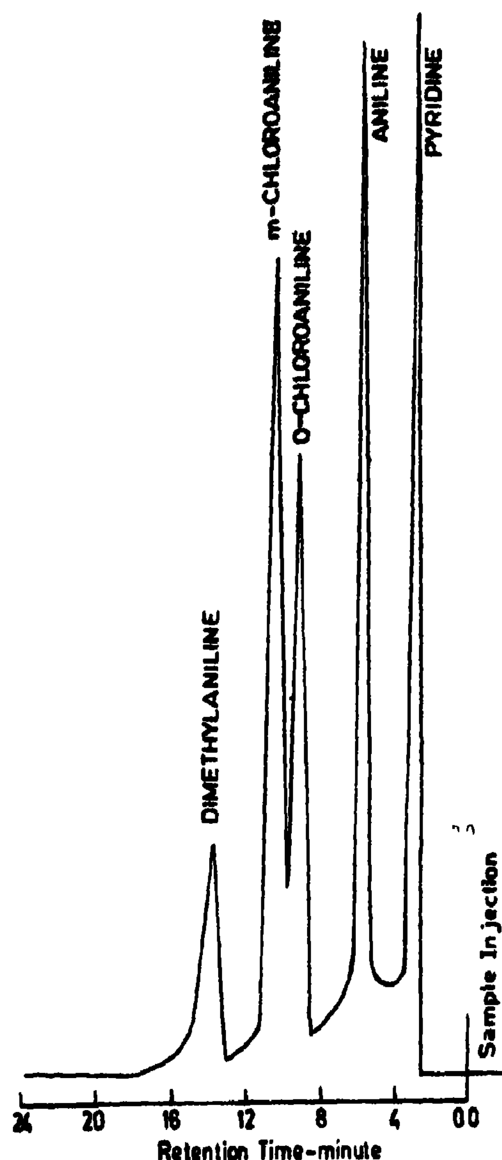


Fig. 9 Chromatogram of a mixture of pyridine, aniline, *o*-chloroaniline, *m*-chloroaniline and dimethylaniline

Column temp. 140°, Flow rate · 30 ml/min, Carrier gas · Nitrogen, separation from a column (2 meter long) containing 15% SE-30 on Diatomite.

(Table 12 contd.)

n-Ethylbenzene	106	136	7.337
n-Propylbenzene	120	159	7.4193
n-Hexanol	102	156	7.6686
Chlorobenzene	112.5	132	8.635
n-Butylbenzene	134	183	9.0068
Bromobenzene	157	156	9.200
n-Heptanol	116	176	9.245
n-Octanol	130	194	9.8026
Iodobenzene	204	188	10.0556
n-Amylbenzene	148	204	10.2442
1-Phenylhexane	162	226	11.500

different compounds have little relation to their boiling points or molecular weights, but are more closely related to their polarisabilities, their abilities to form associations, and are also affected by the spatial structure of the molecules (branching, *o*-, *m*- or *para*-isomerism)[1].

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Kinetics and Mechanism of Oxidation of Substituted Mandelic Acids by Sodium N-chlorobenzenesulphonamide

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The oxidation of mandelic acid and nine monosubstituted mandelic acids by sodium N-chlorobenzenesulphonamide has been studied in aqueous acetic acid and perchloric acid. The reaction is of first order with respect to the concentrations of the oxidant, the hydroxy acid and hydrogen ions. The primary kinetic isotope effect (k_H/k_D) is 5.11±0.06 at 303 K. The solvent isotope effect $[k(H_2O)/k(D_2O)]$ is 0.406 at 303 K. The reaction exhibits a reaction constant $\rho^* = -2.13$ at 303 K. $PhSO_2NHCl$ has been postulated as the active oxidising species. The rates were determined at four temperatures and the activation parameters were evaluated. A mechanism involving transfer of a hydride ion to the oxidant has been suggested.

CHLORAMINE-T (CAT) and N-bromosuccinimide (NBS) are well known organic positive halogen compounds and several reports have appeared on the mechanism of their reactions[1,2]. Another compound of this category is sodium N-chlorobenzenesulphonamide (chloramine-B or CAB). Not much information is available on the mechanism of oxidation by CAB excepting that of alcohols[3]. It is known that reactions of NBS with alcohols and hydroxy acids follow different mechanisms[2,4]. This prompted us to undertake this investigation.

Results and Discussion

The rate laws and other experimental data were obtained for all the substituted mandelic acids. Since results are similar, only those of mandelic acids are described.

Product analysis · Oxidation of mandelic acid by CAB in the presence of $HClO_4$ results in the formation of phenylglyoxylic acid and benzenesulphonamide. Product analysis and stoichiometry determinations indicated the following overall reaction :



$$PhSO_2NCl^- + PhCH(OH)COOH \longrightarrow PhSO_2NH_2 + Cl^- + PhCOCOOH \quad (1)$$

Rate laws : The reaction is of total third order, being first order with respect to CAB, mandelic acid and hydrogen ions. The pseudo-first-order rate constants for varying concentration of one component keeping the concentrations of other components constant are presented in Table 1. When acid strength was varied, ionic strength was kept constant at 1.0 *M* using sodium perchlorate.

Influence of radical traps : The reaction is not affected by added radical scavengers like allyl acetate as allyl acetate, up to 0.02 *M*, did not affect the oxidation rate. The oxidation of mandelic acid in an atmosphere of nitrogen failed to induce polymerisation of acrylonitrile.

Isotope effects : Experiments were conducted with α-deuteriomandelic acid [PhCD(OH)COOH]

TABLE 1—RATE CONSTANTS FOR THE OXIDATION OF MANDELIC ACID BY CAB AT 303 K

[MA] *M*	[CAB] *M*	$[H^+]$ *M*	$10^4 k_1$, sec^{-1}
0.05	0.005	0.5	3.08
0.10	0.005	0.5	6.00
0.20	0.005	0.5	12.0
0.40	0.005	0.5	23.8
0.50	0.005	0.5	31.0
0.20	0.010	0.5	11.9
0.20	0.020	0.5	12.3
0.20	0.030	0.5	12.2
0.10	0.005	0.1	1.25
0.10	0.005	0.2	2.60
0.10	0.005	0.3	3.80
0.10	0.005	0.4	5.18

to ascertain the importance of cleavage of C–H bond in the rate-determining step. The primary kinetic isotope effect, k_H/k_D, has a value of 5.11± 0.06 at 303 K (Table 2).

TABLE 2—KINETIC ISOTOPE EFFECT IN THE OXIDATION OF MANDELIC ACID

[CAB]=0.005 *M* , $[H^+]$=0.5 *M* , Temp.=303 K

[MA] *M*	Type	$10^4 k_1$, sec^{-1}	
0.05	H	3.08	
0.10	H	6.00	$10^4 k_H = 12.0 \pm 0.1\ l^2\ mole^{-2}\ s^{-1}$
0.20	H	11.9	
0.10	D	1.18	
0.20	D	2.35	$10^4 k_D = 2.35 \pm 0.02\ l^2\ mol^{-2}\ s^{-1}$
0.30	D	3.50	

$k_H/k_D = 5.11 \pm 0.06$

The oxidation of mandelic acid was studied in 95% deuterium oxide. The rate constants for the oxidation in H_2O and D_2O at 303 K are $10^4 k =$ 4.67 and 11.5 $l^2\ mol^{-2}\ s^{-1}$, respectively. The

solvent isotope effect, $k(H_2O)/k(D_2O) = 0.406$. In this set of experiments acetic acid was not added to the solvent.

Dependence on solvent composition : The effect of variation of solvent composition on the oxidation rate has been studied in binary mixture of acetic acid and water. The reaction rate increases slightly with increasing proportion of acetic acid in the solvent (Table 3).

TABLE 3—DEPENDENCE OF THE REACTION RATE ON SOLVENT COMPOSITION

[MA] = 0.10, [CAB] = 0.005 *M*, $[H^+]$ = 0.5, Temp. = 308 K

Percentage of acetic acid (v/v)	0	20	35	50	60
$10^4 k_1$, sec^{-1}	2.84	3.71	4.60	6.00	7.75

Addition of benzenesulphonamide (up to 0.05 *M*) did not affect the reaction rate.

Influence of substituents : The effects of *m*- and *p*-substituents in the mandelic acid molecule on the oxidation rate have been studied with nine different mono-substituted compounds. The rates were obtained at different temperatures between 303-318 K and the activation parameters were calculated (Table 4). The average error limits in the values of ΔH^*, ΔS^* and ΔG^* (at 303 K) are ± 4 kJ mol^{-1}, ± 6 J mol^{-1} K^{-1} and ± 5 kJ mol^{-1} respectively.

TABLE 4—RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF SUBSTITUTED MANDELIC ACIDS BY CAB

Substituent	$10^4 k$ l^2 mol^{-2} sec^{-1} 303	308	313	318 K	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔG^* kJ mol^{-1}
H	120	173	250	362	61.4	128	100
p-F	85.2	125	184	274	64.8	120	101
p-Cl	69.2	103	155	234	65.1	117	101
p-Br	58.3	87.4	123	202	67.4	118	103
p-Et	501	660	864	1140	44.0	166	94.0
p-Pr^i	468	614	808	1070	44.7	164	94.4
p-OMe	5490	6810	6940	7820	21.6	228	90.7
m-Cl	18.6	28.6	47.3	77.7	78.7	88.5	105
m-NO_2	4.47	7.90	14.4	25.8	96.3	40.9	108
p-NO_2	2.63	4.76	9.02	16.7	102	27.4	110

Not much information is available about the equilibria present in acidified CAB solution, though the same have been reported in detail for CAT in acid solution[5-8]. Assuming that CAB behaves like CAT, the following equilibria are possible in acidified CAB solution (where R = $PhSO_2$) :



$$RNCl^- + H_3O^+ \rightleftharpoons RNHCl + H_2O \quad (2)$$



$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \quad (3)$$



$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \quad (4)$$



$$RNCl_2 + 2H_2O \rightleftharpoons RNH_2 + 2HOCl \quad (5)$$

The probable oxidising species are RNHCl, $RNCl_2$ and HOCl. Soper[8] has shown that the concentration of HOCl in acidified CAT is very small and is independent of CAT concentration. The predominant species is TsNHCl and the concentration of $TsNCl_2$ is proportional to that of TsNHCl. Thus one can conclude that the relative amounts of the probable oxidising species will not change with CAB concentration and the reaction will show first order dependence on CAB inspite of the variety of species present. However, dichloramine-B ($RNCl_2$) can be ruled out as the reactive species in view of the strict first order dependence on CAB. In the reaction of related sodium N-bromobenzenesulphonamide the effect of HOBr was observed as an initial deviation in the kinetic curve, before its contribution was stifled by the product benzenesulphonamide[9]. Initially added benzenesulphonamide eliminated this deviation. In the present investigation no deviation was observed in the kinetic curve. Thus, any role of HOCl even in the initial stages of the reaction is unlikely. Further, no effect of benzenesulphonamide on the reaction rate precludes both HOCl and $RNCl_2$ as the oxidising species. This leaves RNHCl or $PhSO_2NHCl$ as the most probable oxidising species. This supports the conclusion of Ruff and Kucsman[10] that in the oxidation of organic sulphides by CAT in strongly acidic solvents, TsNHCl alone is the reactive species.

The increase in the amount of acetic acid in the solution decreases the polarity of the solvent and favours reactions in which uncharged molecules are formed from ion[11]. Therefore, the equilibrium (2) is favoured by solvent with increasing amounts of acetic acid which may explain the observed rate enhancement

The large primary kinetic isotope effect confirms that the rate-determining step involves cleavage of C - H bond from the carbon bearing the functional groups.

The activation enthalpies and entropies of the ten compounds are linearly related (r = 0.9990). The correlation was tested and found genuine by applying Exner's criterion[12]. The isokinetic temperature computed from the plot is 407 K. Current views do not attach much physical significance to isokinetic temperature[13], though a linear correlation is usually a necessary condition for the validity of linear free energy relationships.

An insight into the transition state of the oxidation may be obtained from the analysis of the effect of substituents on the reaction rate. The introduction of electron-withdrawing groups decreases the rate of oxidation while electron-donating groups have reverse effect. The oxidation rates correlate very well with Brown's σ^+ values[14] with large negative reaction constants. The values of reaction constant, ρ^+, are -2.13 (r = 0.9935), -2.00 (r = 0.9933), -1.85 (r = 0.9934) and -1.71 (r = 0.9933) at 303 K, 308 K, 313 K and 318 K, respectively. The negative values of ρ^+ indicate an electron-deficient carbon centre in the transition state.

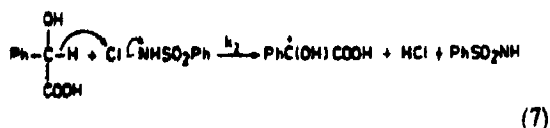
A hydrogen abstraction mechanism may be discounted in view of the nil effect of radical

scavengers and the magnitude of the reaction constant. In most reactions involving hydrogen abstraction, the reaction constants have small magnitudes[14]. The large negative reaction constant together with the substantial deuterium isotope effect indicate a considerable carbonium ion character in the transition state. The above results suggest a hydride ion transfer in the rate-determining step.

Natarajan and Thiagarajan[15] suggested formation of a hypochlorite ester as the rate-determining step in the oxidation of 2-propanol by CAT in acid solution. However, the observed solvent isotope effect does not indicate any involvement of the hydroxyl either in the rate-determining step or in the pre-equilibria. Correlation with σ^+ values also suggests an intermolecular hydride ion transfer. The observed kinetic isotope effect is also rather large for the non-linear transition state implied in the ester mechanism. The following mechanism may then be proposed.



$$PhSO_2NCl^- + H_3O^+ \overset{K}{\rightleftharpoons} PhSO_2NHCl + H_2O \quad (6)$$



$$Ph-\underset{COOH}{\overset{OH}{C}}-H + Cl-NHSO_2Ph \xrightarrow{k_2} Ph\overset{+}{C}(OH)COOH + HCl + PhSO_2NH^- \quad (7)$$



$$PhSO_2NH^- + HCl \xrightarrow{fast} PhSO_2NH_2 + Cl^- \quad (8)$$



$$Ph\overset{+}{C}(OH)COOH \xrightarrow{fast} PhCOCOOH + H^+ \quad (9)$$

The following rate equation may be derived for the above mechanism :

$$-d[PhSO_2NCl^-]/dt = k_2[PhSO_2NHCl][MA] \quad (10)$$

$$= k_2K[PhSO_2NCl^-][H_3O^+][MA] \quad (11)$$

where MA = mandelic acid

Eq. (11) requires that the reaction should exhibit a first order dependence on CAB, the hydroxy acid and hydrogen ions. This agrees with the experimentally derived rate laws.

Experimental

Materials : The preparations and specification of the mandelic acids have been described earlier[16]. The isotopic purity of α-deuteriomandelic acid, as ascertained by its nmr spectrum was 92±5%. Chloramine-B was prepared by chlorination of an alkaline solution of benzenesulphonamide[17]. The crude product was recrystallised from hot water. The purity was checked by determining the amount of active chlorine iodometrically. Acetic acid was purified by usual methods[18]. Perchloric acid was used as a source of hydrogen ions.

Product analysis and stoichiometry : Mandelic acid (7.6 g ; 0.05 mol) and CAB (2.1 g ; 0.01 mol) were made up to 100 ml in 1 : 1 (v/v) acetic acid-water, in the presence of 0.5 *M* perchloric acid. The reaction mixture was kept in the dark for *ca* 10 hr to ensure completion of the reaction. It was treated overnight with an excess (250 ml) of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallised from ethanol, and weighed again. Determination of mixed m.p. and mixed tlc with an authentic sample of DNP confirmed that the product is phenylglyoxylic acid. The yields of DNP before and after recrystallisation were 2.6 g (78%) and 2.3 g (70%) respectively.

Stoichiometry was ascertained by treating mandelic acid (1.52 g ; 0.01 mol) with CAB (10.5 g ; 0.05 mol) in the presence of 0.5 *M* perchloric acid in 1 : 1 (v/v) acetic acid-water. The residual CAB was determined iodometrically. Several determinations with various hydroxy acids indicated a 1 : 1 stoichiometry.

Other experimental details have been described earlier[8].

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Photochemical and Thermal Transformations of S-Benzoyl-O-alkyl Xanthates

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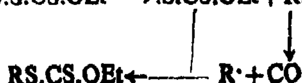
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The reaction of benzoyl chloride with different potassium-O-alkyl xanthates (n-propyl, iso-propyl, n-butyl) around 0° afforded good yields of corresponding S-benzoyl-O-alkyl xanthates. The structure of these aroyl xanthates were consistent with the spectral data. Aroyl xanthates have been reported to be resistant to photolysis. It has, however, been observed in the present investigation that the fragmentation of these S-benzoyl-O-alkyl xanthates does occur on prolonged photolysis. Irradiation of these xanthates in benzene solution with mercury lamp for 60-70 hr resulted in the formation of benzoyl disulfide. Thermal decomposition around 250° for 15 min gave benzoyl disulfide, corresponding ester and carbon disulfide.

PHOTOCHEMICAL and thermal transformations of a few acyl xanthates have been reported by Barton *et al*[1], who observed that alkane and arylalkanecarbonyl xanthates are decomposed by light. Thus for example, irradiation of O-ethyl-S-phenyl acetyl xanthate in benzene solution under reflux gave S-benzoyl-O-ethyl xanthate in high yield. It has been suggested that the photolysis of acyl xanthates proceed through a free radical pathway involving the initial fragmentation of a C–S bond, resulting in the formation of acyl and xanthate radicals.





A similar type of fragmentation has been reported in the photolysis of several acyl xanthates[2], phthaloyl dixanthates[3,4], phthaloic *bis* dithiocarbamic anhydride[4], O-alkyl-S-phthalyl xanthates[5] and dithiocarbamoyl phthalides[5].

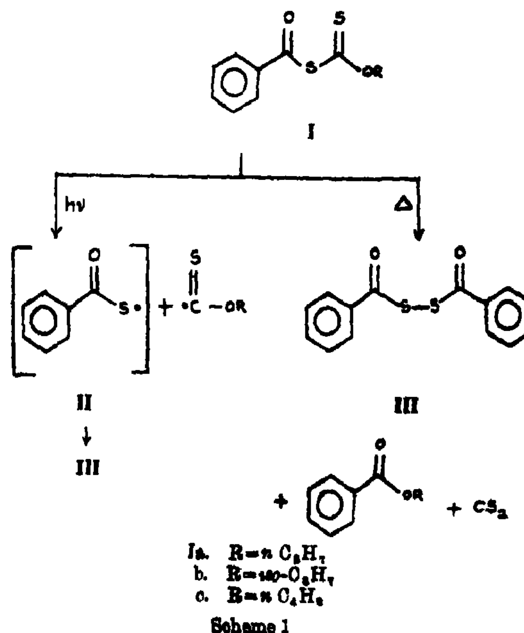
S-benzoyl and S-*p*-chloro benzoyl-O-ethyl xanthates were reported[1] to be resistant to photolysis in boiling benzene or toluene due to the stability of ArCO radical formed during photolysis.

The object of the present investigation was to examine both the photochemical and thermal transformations of a few aroyl xanthates, with a view to studying the nature of the products formed in these reactions and the mode of fragmentation. In this connection we have studied the reaction of benzoyl chloride with different potassium-O-alkyl xanthates.

Treatment of an acetone solution of benzoyl chloride around 0° with potassium-O-alkyl xanthates gave S-benzoyl-O-alkyl xanthates (Ia-c) in good yield.

The structural assignment of Ia-c were consistent with the spectral data. The ir spectrum of these aroyl xanthates showed prominent bands at 1700 and 1270 cm^{-1} due to the presence of C=O and C=S groups, respectively. The uv spectrum showed a weak absorption band at 410 nm, characteristic of aroyl xanthates.

Photolysis of the xanthates (Ia-c) in dry benzene for 60-70 hr with a mercury lamp in a pyrex flask gave a gummy solid from which only benzoyl disulfide could be isolated. A probable mechanism consistent with the formation of this product is shown in Scheme 1.



Scheme 1

The free-radical pathway involving a C(S)–S bond fission resulting in the free radical II and subsequent dimerisation explains the formation of III. Benzoyl disulfide thus formed has been reported to be resistant to photolysis[6]. However,

earlier workers have reported the formation of free-radicals due to the C(O)–S bond fission[1,8]. Our attempts to isolate benzil from the reaction mixture were not successful, which indicates that the aroyl radical formed during the photolysis does not dimerise.

The thermal decomposition of aroyl xanthates have been reported to be much more complex[1,7]. Thus, thermal decomposition of O-ethyl-S-benzoyl xanthate at 18 mm has been reported to give a mixture of benzoyl disulfide, ethyl benzoate, ethyl thiobenzoate, ethyl dithiobenzoate and tetraphenyl thiophene nonasulfide[7]. Barton *et al* have reported the thermal decomposition of acyl xanthates around 200° to give esters and carbon disulfide[1]. A four membered cyclic transition state has been suggested for such decomposition[1,6]. Pyrolysis of xanthates (Ia-c) around 250° for 15 min gave benzoyl disulfide, corresponding esters and carbon disulfide as shown in Scheme 1.

Experimental

IR spectra were recorded on Beckman IR-20 Infrared spectrophotometer and uv spectra were recorded on Specord UV spectrophotometer Potassium-O-*n*-propyl xanthate, m.p. 230°, potassium-O-isopropyl xanthate, m.p. 274°, and potassium-O-*n*-butyl xanthate, m.p. 258° were prepared by known procedure[9]. TLC was run on silica gel using methylene chloride-petroleum ether (1 . 1) as eluent.

Reaction of benzoyl chloride with potassium-O-alkyl xanthate ·

Ia : Benzoyl chloride (1.40 g ; 0.01 mole) was taken in acetone (20 ml) and to this was added potassium-O-*n*-propyl xanthate (1.74 g ; 0.01 mole) portion-wise with constant stirring at 0° during 30 min. Stirring was continued for additional 30 min at room temperature. Filtration of precipitated potassium chloride and removal of the solvent under vacuum gave a residue which was dissolved in methylene chloride (25 ml) and washed with 1% $NaHCO_3$ solution.

The methylene chloride extract was repeatedly washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent gave 2.26 g (94%) of S-benzoyl-O-*n*-propyl xanthate (Ia) as a yellow liquid, n_D^{28} 1.6010 ; uv : $\lambda_{Max}^{Ethanol}$ 215 (ϵ, 13,740), 245 (ϵ, 19,200), 280 (ϵ, 10,260) and 410 nm (ϵ, 76) ; ir : 1700 cm^{-1}(C=O), 1270 cm^{-1} (C=S). This xanthate was unstable and satisfactory analytical data were not secured for this compound.

Ib : Similarly, S-benzoyl-O-isopropyl xanthate (Ib) in 51% yield was obtained as a yellow liquid, n_D^{28} 1.5010 ; uv : $\lambda_{Max}^{Ethanol}$ 215 (ϵ, 9,000), 245 (ϵ, 12,800), 290 (ϵ, 5,650) and 410 nm (ϵ, 39) ; ir : 1700 cm^{-1} (C=O), 1380 cm^{-1} ($-HC\langle^{CH_3}_{CH_3}$), 1270 cm^{-1} (C=S). (Found : C, 55.58 ; H, 5.27. $C_{11}H_{12}O_2S_2$ requires C, 55.0 ; H, 5.0%)

Ic : Similarly, S-benzoyl-O-*n*-butyl xanthate (Ic) in 56% yield was obtained as a yellow liquid n_D^{28} 1.5940 ; uv : $\lambda_{Max}^{Ethanol}$ 215 (ϵ, 12,192), 250 (ϵ, 14,859), 285 (ϵ, 12,192) and 410 nm (ϵ, 96) ; ir : 1700 cm^{-1} (C=O), 1270 cm^{-1} (C=S).

This xanthate was unstable and satisfactory analytical data were not secured for this compound.

Photochemical transformation of S-benzoyl-O-alkyl xanthate .

Ia · A solution of the xanthate Ia (1.00 g) in dry benzene (A.R ; 35 ml) was irradiated for 70 hr with mercury lamp in a pyrex flask. Removal of the solvent gave a gummy solid. Trituration with petroleum ether resulted in 75 mg of benzoyl disulfide, m.p. 129° (m.m.p.)[10]. A solution of the xanthate Ia subjected to similar conditions in the absence of light did not show any appreciable change.

Similarly, the photolysis of Ib (1.00 g) and Ic (2 02 g) in benzene solution gave benzoyl disulfide as the only isolable product in yield 115 mg and 205 mg, respectively

Thermal decomposition of S benzoyl-O-alkylxanthate,

Ia : The xanthate Ia (3.50 g) was heated under continuous stream of nitrogen in an oil bath maintained at 250° for 15 min. The gaseous product was trapped by passing it in piperidine solution (in methylene chloride) which gave 1.30 g of piperidinium cyclopentamethylenedithiocarbamate, m p. 169° (lit. m.p. 169°)[8], corresponding to 36% yield of carbon disulfide. The residual brown mass was triturated with petroleum ether and the solid thus separated was filtered and recrystallised from a mixture of methylene chloride and petroleum ether to give 0.21 g of benzoyl disulfide, m.p. 129° (m.m p)[10]. The residual mass was hydrolysed with 10% aq. KOH to give 0.28 g of benzoic acid, m.p.119° (m.m.p) corresponding to 16% yield of *n*-propylbenzoate.

Ib : Similarly, heating Ib (3.13 g) at 250° for 15 min gave 1.02 g of piperidinium cyclopentamethylenedithiocarbamate, m.p. 169°, corresponding to 34% yield of carbon disulfide, and 0.43 g of benzoyl disulfide, m.p. 129°. Hydrolysis of residual mass gave 0.360 g of benzoic acid, m.p. 119° corresponding to 17% yield of isopropylbenzoate.

Ic : Similarly, heating Ic (3.60 g) at 250° for 15 min gave 1.98 g of piperidinium cyclopentamethylenedithiocarbamate, m.p. 169° corresponding to 57% yield of carbon disulfide and 0.21 g of benzoyl disulfide, m.p. 129°. Hydrolysis of the residual mass gave 0.40 g of benzoic acid, m.p. 119° corresponding to 23% yield of *n*-butyl benzoate.

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Carbon-13 NMR Signals of Some Phenothiazine Derivatives

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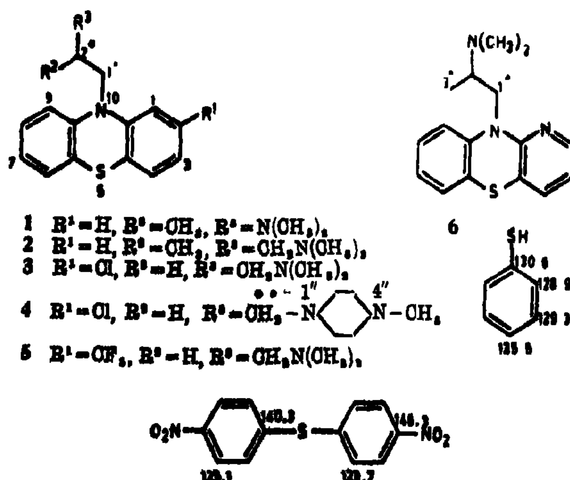
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Carbon-13 nmr signal assignments of the CNS depressants promethazine (1), trimeprazine (2), chlorpromazine (3), prochlorperazine (4), triflupromazine (5), isothiopendyl (6) and some of their salts are reported. C–H coupling constant (^1J and ^3J) measurements have also been made.

THE carbon-13 nmr spectral studies of various synthetic and natural therapeutic agents are of current interest[1-3]. We report here the carbon-13 nmr spectral assignments of the drugs promethazine [10-(2-dimethylaminopropyl)phenothiazine] (1), trimeprazine [10-(3-dimethylamino-2-methylpropyl)-phenothiazine] (2), chlorpromazine [2-chloro-10-(3-dimethylaminopropyl)phenothiazine] (3), prochlorperazine {2-chloro-10-[3-(4-methyl-1-piperazinyl)propyl]phenothiazine} (4), triflupromazine [10-(3-dimethylaminopropyl)-2-trifluoromethyl-phenothiazine] (5) and isothiopendyl [10-(2-dimethylaminopropyl)-1-azaphenothiazine] (6) and some of their salts. These compounds are well known for their tranquillizing activity[4] and their ^{13}C nmr spectral studies are of biological as well as of theoretical interest. The assignment of the resonances in the spectra of 1 - 6 and some of their salts were made by considering the chemical shift theory[5,6] and is presented in Table 1.

Promethazine (1) displayed four signals at δ 115.5, 122.3, 126.9 and 127.3 for the eight unsubstituted aromatic carbons. A comparison of the resonance positions of the various carbons of thiophenol and 4,4'-dinitrodiphenylsulphide with those of benzene[5] and nitrobenzene[5], respectively indicated that the thioether function in the former compounds had little effect on the chemical shifts of the aromatic carbons. Thus it is quite likely that C-1 (as well as C-9) in 1 should be associated with the signal at δ 115.5 and consequently C-3 (and C-7) with the resonance at δ 122.3. The resonances at δ 126.9 and 127.3 should thus be related to C-2 (and C-8) and C-4 (and C-6). Similarly the substituted aromatic carbon signals at δ 125.6 and 145.3 in 1 should be assigned to C-4a (and C-5a) and C-9a (and C-10a), respectively. Trimeprazine (2) also exhibited similar resonances for aromatic carbons as those in 1. The effect of incorporation of a chlorine atom or a trifluoromethyl group at C-2 position in the phenothiazine nucleus as in chlorpromazine (3) and prochlorperazine (4) or in triflupromazine (5) on the chemical shifts of the different carbons in ring A was according to the shift theory[5,6]. In addition to the resonances at δ 115.6, 122.8, 127.0 and 127.3 for C-9, C-7, C-8 and C-6, three more unsubstituted aromatic carbon resonances at δ 117.6, 134.1 and 144.7 were present in the spectra of isothiopendyl (6). These signals should be readily related to C-3, C-4 and C-2, respectively. Of the four substituted aromatic carbon resonances at δ 117.7, 122.1, 142.8 and 155.2 exhibited by 6, the last one must be associated with C-10a and consequently the signal δ 142.8 was linked with C-9a. The C-5a should be associated with the signal at δ 122.1 from the similarity of the resonance position of C-5a in related compounds 1-5. Thus C-4a was assigned the δ 117.6 resonance.



The resonances for the side chain carbons in 1 were readily accounted for from the splitting pattern in the SFORD spectrum and chemical shift theory. The shift of the $-N(CH_3)_2$ group from C-2' position to C-3' position should cause high field movement of C-1' resonance. Thus C-1' in 3 was related to the signal at δ 45.2. The signal for C-1', C-2' and C-3' in 2 appeared at low field positions compared to the resonance positions for these carbons in 3 due to the deshielding effect of the methyl group at C-2' in 2. C-2'' and C-6'' in 4 was linked to δ 52.8 resonance since it experienced more shielding γ-effect than C-3'' and C-5'' (δ 54.7).

In the spectra of the salts of 1, 2, 3, 5 and 6 small deshielding of aromatic carbons were observed, the substituted aromatic carbons being

TABLE 1—CARBON-13 CHEMICAL SHIFTS (δ) AND COUPLING CONSTANTS (Hz) OF THE PHENOTHIAZINE DRUGS 1-6 AND THEIR SALTS

Carbon	Promethazine (1)[a]		Trimeprazine (2)[b]		Chlorpromazine (3)[a]		Prochlorperazine (4)		Triflupromazine (5)[a]		Isothiopendyl (6)[a]	
	Shift	^1J(CH), ^3J(CH)	Shift	^1J(CH), ^3J(CH)	Shift	^1J(CH), ^3J(CH)	Shift	^1J(CH), ^3J(CH)	Shift	^1J(CH), ^3J(CH)	Shift	^1J(CH), ^3J(CH)
1	115.5 (117.3)	159.0, 7 8 (162.0)	115 8 (117.4)	159.0, 7 2 (162 1)	115 6 (116.8)	163 4 4 5	115 4	163 1 4 5	111.6 (112.8)	159.8 (159.1)		
2	126.9[c] (128.6)[d]	161.4, 7.8 (161.8)	126.9[c] (128.3)[d]	161 0, 7 9 (161 6)	132 9 (133.9)		132.7		118.5 (118.2)		144.7 (145.6)	178.7, 7.4 (180.1)
3	122.3 (124.4)	162.7, 7 2 (164 0)	122 2 (123 9)	162.7, 7 4 (164.8)	122 6[c] (123.3)	163 2, 7 4	122.4[c]	163 1 7 4	118 7 (119.7)	163.3, 7.5 (162.3)	117.6 (120.1)	166.0, 8.7 (168.5)
4	127.3[c] (129.1)[d]	161.2, 8 1 (161 8)	127.3[c] (128 8)[d]	160.9, 7 9 (161 6)	127 5 (129 1)	163 9	127 4	163 9	127 3 (128.4)	164.2 (163.7)	134.1 (136.3)	162.9, 6.7 (168.0, 7.7)
4a	125.6 (126.4)		125.7 (126.2)		123 3 (124.2)		123.0		129.8 (130.7)		117.6 (119.3)	
5a	125.6 (126.4)		125 7 (126.2)		124 5 (125 2)		124 2		123.9 (124 2)		122.1 (122.2)	
6	127.3[e] (129.1)[f]	161 2 8 1 (161.8)	127.3[e] (128 8)[f]	160.9, 7 9 (161 6)	127.1 (128.5)[d]	161.7, 8.1	127 0	161 6, 7.7	127.4[c] (129.2)[d]	160.4, 6 3 (161.4)	127.3[c] (129.4)[d]	161.9, 7.3 (160.5)
7	122.3 (124.4)	162 7, 7 2 (164 0)	122.2 (123 9)	162 7, 7.4 (164 8)	121 9[c] (124 2)	168 9, 5 1	121.7[c]	168.8, 5 0	122.9 (124 2)	163.3, 7.5 (163.2)	122.8 (124.9)	162.9, 6.8 (162.1)
8	126.9[e] (128.6)[f]	161.4, 7.8 (161.8)	126.9[e] (128 3)[f]	161.0, 7 9 (161 6)	127 1 (128 6)[d]	161 7, 8 1	127.0	161 6, 7 7	127 3[c] (128.2)[d]	160.4, 6 3 (163.7)	127.0[c] (128.0)[d]	162.5, 6 6 (160.4)
9	115.5 (117.3)	159.0, 7.8 (162.0)	115 8 (117 4)	159.0, 7 2 (162 1)	115.6 (117 4)	160.2, 7 7	115.4	159 7, 8 0	115.7 (117.5)	159.3, 8.1 (161 8)	115.6 (116.9)	159.0, 7 2 (157.5)
9a	145 3 (145.0)		145 5 (145 8)		144.1 (144 2)		144.0		144.1 (143.8)		142.8 (142.8)	
10a	145.3 (145.0)		145 5 (145 8)		146.2 (147.0)		146.0		145.4 (146.2)		155.2 (154.8)	
1′	50.5 (47.8)	137 8 (143.0)	52 0 (51.2)[g]	136 5	45 2 (44.6)	135.7	44.9	135 4	45 2 (44.5)	136.4 (140.2)	46.4 (47.2)	139.0 (139.8)
2′	55.7 (59.4)	135.0 (146.1)	28.6 (27 7)	125.7 (125.2)	24.6 (22.4)	129.0	23 8	129 8	24 5 (22.4)	128.0 (129.2)	56.2 (61.3)	132.2 (148 9)
3′	12.1 (12.7)	125.1, 3.8 (130.6)	64.6 (62.6)[g]	135 7	56.5 (55.7)	135.0	54.9	134.3	56.6 (55 7)	135.0 (136.9)	12.2 (12.2)	125.9, 3.5 (128.9)
N–CH₃ or N(CH₃)₂	40.7 (40.4)	133.1, 4.9 and 5.2 (142.8)	45.8 (44 0)	133.8 (143 0)	45 1 (43 4)	131.6	45.6	132.5	45.0 (43 4)	133 9, 4 9 (143.6)	40.6 (40 9)	133.5, 4 9 and 4.8 (144 0)
2′-CH₃			16.8 (16.1)	126.7 (128 2)								
2″, 6″							52.8	133.6				
3″, 5″							54 7	131.1				

a. Values for the hydrochloride salt are given in the parentheses

b. Values for the tartrate salt are given in the parentheses, CH(OH) δ 74 7, COOH δ 178.9

c,d,e,f. Values along the vertical column are interchangeable

g. In the coupled spectra the signals were very weak.

relatively less influenced. C−2′ in 1 and 6 salts were deshielded appreciably but some side chain carbons experienced small shielding effects in the corresponding salts.

Experimental

The carbon-13 nmr spectra were recorded on a Varian Associates CFT-20 NMR spectrometer operating at 20.1 MHz in the FT mode The compounds were submitted to PND, SFORD and noise coupling with nOe to establish the carbon shifts, degree of protonation and *J* values The samples were run in 10 mm o.d tubes using $CDCl_3$ as solvent as well as internal lock and internal standard. The spectra of the salts were taken in D_2O serving as solvent and internal lock while dioxan was used as internal standard. All solutions were *ca* 10-15% in concentration. The chemical shifts reported are in δ (ppm) downfield from TMS ; $\delta_{TMS} = \delta_{CDCl_3} + 76.9$ ppm $= \delta_{Dioxan} + 67.4$ ppm. The spectra were run with sweepwidth 4000 Hz, pulsewidth 10 μs (approximately 45° tilt angle) and about 2 s delay in between pulses

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A Novel Route to the Synthesis of 3-Arylimino-5-p-Methoxyphenyl-1,2,4-Dithiazoles. Part—III

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The synthesis of a series of a new 3-arylimino-5-p-methoxyphenyl-1,2,4-dithiazoles (IV) has been described by the oxidative debenzylation and cyclisation of S-benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamide (II) with bromine in concentrated chloroform solution. The structure of these dithiazoles (IV) has been confirmed by their comparison with the compounds obtained by the direct oxidation of the corresponding N-arylthiocarbamoyl-p-methoxythiobenzamide (III).

A couple of methods have been used for the synthesis of substituted 1,2,4-dithiazoles[1,2]. Earlier, we reported the synthesis of some of these heterocycles[3,4] by the interaction of thiocarbamoylthioamides with bromine. Here we report the synthesis of some new S-benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamides and their elaboration to certain novel heterocycles i.e., 3-arylimino-5-p-methoxyphenyl-1,2,4-dithiazoles.

The thiohydrolysis of p-methoxybenzonitrile afforded p-methoxythiobenzamide, which was benzylated with benzylchloride in presence of sodium methoxide. The resulting S-benzyliso-p-methoxythiobenzamide was subjected to reaction with appropriate arylisothiocyanate to yield the corresponding S-benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamide (II). The chloroform solution of the latter was treated with bromine, when the benzyl group was eliminated as benzylbromide followed by ring closure to the related 3-arylimino-5-p-methoxyphenyl-1,2,4-dithiazoles (IV). These dithiazoles have also been obtained by the oxidation of the corresponding N-arylthiocarbamoyl-p-methoxythiobenzamide (III), which were obtained by the reductive debenzylation of the related S-benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamide (II) with hydrogen sulphide in pyridine-triethylamine[4] and also by reduction of IV under identical conditions. The structural assignments of the compounds III and IV were rationalized by their synthyesis through alternative routes as described above.

The ir spectra of compounds II and III showed characteristic absorption in the region around 3150-3400 cm^{-1} and 1470-1500 cm^{-1} indicating –NH stretching[5,6] and –N–C(=S)–N– grouping[6], respectively. A weak absorption in the region 1600-1640 cm^{-1} and strong absorption at 1250 cm^{-1} were recorded due to –NH[6] and –C–NH.Ar[6] deformation vibration of compounds II and III. In compounds III, the absorption at 1370 cm^{-1} showed the presence of –C=S grouping[7-10]. The compounds IV were characterised by the absorption appearing at 1620 cm^{-1} (–C=N– grouping)[7-9], 1350-1500 cm^{-1} (ring –C–S– stretching)[7] and 480-510 cm^{-1} (–S–S– linkage)[7,8], respectively. The scheme of the reactions can be outlined as given on next page.

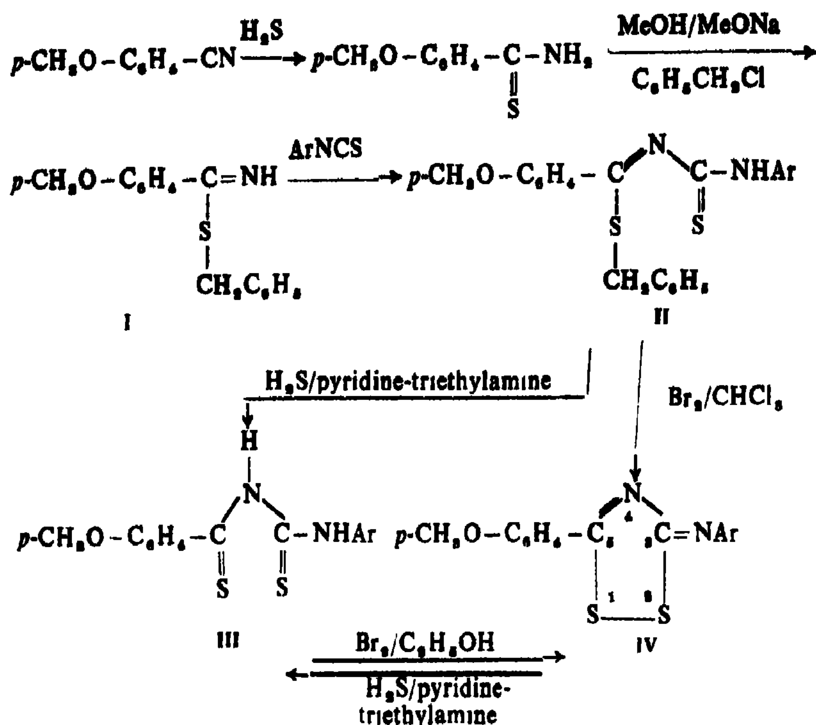
* For correspondence.

Experimental

Melting points of all the compounds are taken by open capillary tube method and are uncorrected. IR spectra were run in Nujol on Perkin-Elmer model 720-Infrared spectrophotometer. p-Methoxythiobenzamide was prepared according to known methods.

S-Benzylisothiobenzamide (I): p-Methoxythiobenzamide (5 g; 0.03 mole) was benzylated with benzylchloride (3.75 g, 3.4 ml; 0.03 mole) in presence of sodium methoxide (1.61 g; 0.03 mole) using methanol (25 ml) as solvent. The reaction mixture was stirred for 3 hr with gentle heating and was allowed to stand overnight. It was refluxed for 15 min. Solvent was evaporated under reduced pressure and the residue was extracted with benzene and dried over anhydrous calcium chloride. The evaporation of excess benzene gave the expected S-benzyliso-p-methoxythiobenzamide, yield 4.0 g (52%), crystallised from ethanol, m.p. 130°.

S-Benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamides (II) ($Ar=C_6H_5$): The details of a typical experiment are given below. S-Benzyliso-p-methoxythiobenzamide (5 g; 0.019 mole) was refluxed with phenylisothiocyanate (2.62 g; 0.019 mole) and 30 ml of 10% sodium hydroxide solution for 2 hr. The resulting mixture was extracted with benzene and the benzene extract was further heated under reflux for 1 hr. After evaporation of excess of benzene, the resulting mass was washed with petroleum ether (40-60°) and a little ethanol added



where Ar = phenyl-, p-tolyl-, p-chlorophenyl-, p-methoxyphenyl-, p-ethoxyphenyl- groups

Scheme of the reactions

to give the expected S-benzyliso-N-phenylthiocarbamoyl-*p*-methoxythiobenzamide (II). It was crystallised from ethanol, yield 3.0 g (40%), m.p 145°. The results are given in Table 1.

TABLE 1—S-BENZYLISO-N-ARYLTHIOCARBAMOYL-*p*-METHOXYTHIOBENZAMIDES (II)

Ar	Molecular formula	m p °C	Yield (%)	Analysis Calcd	Found
C_6H_5 -	$C_{22}H_{20}N_2S_2$	145	40	C, 67.34	67.02
				H, 05.10	04.90
p-$H_3CC_6H_4$ -	$C_{23}H_{22}N_2S_2$	176	60	C, 67.98	68.01
				H, 05 41	05.21
p-ClC_6H_4 -	$C_{22}H_{19}N_2S_2Cl$	175	55	C, 61.89	62.00
				H, 04.45	04.50
p-$MeOC_6H_4$ -	$C_{23}H_{22}N_2S_2O$	170	52	C, 65.40	65.09
				H, 05.21	05.22
p-$EtOC_6H_4$ -	$C_{24}H_{24}N_2S_2O$	165	61	C, 66.05	65.08
				H, 05 50	05.56

3-Arylimino-5-p-methoxyphenyl-1,2,4-dithiazoles (IV) : (*i*) *Oxidative debenzylation and cyclisation of S-benzyliso-N-arylthiocarbamoyl-p-methoxythiobenzamides* : Details of typical experiment are as follows: S-Benzyliso-N-phenylthiocarbamoyl-*p*-methoxythiobenzamide (II. Ar = C_6H_5) (5 g ; 0.012 mole) moistened with a little chloroform (2 ml) was treated with small amounts of neat bromine till the colour of bromine persisted. The evolution of lachrymatory fumes of benzylbromide indicated the completion of the debenzylation reaction. The reaction mixture was allowed to stand for 1 hr and thereafter washed thoroughly with ether. The treatment of the resulting residue with a little ethanol afforded the desired 3-phenylimino-5-*p*-methoxyphenyl-1,2,4-dithiazole hydrobromide which on basification with ammonia gave the corresponding free base. It was crystallised from ethanol, yield 2.5 g (65%), m.p. 168°. The results are presented in Table 2.

TABLE 2—3-ARYLIMINO-5-*p*-METHOXYPHENYL-1,2,4-DITHIAZOLES (IV)

Ar	Molecular formula	m.p °C	Yield (%)	Analysis Calcd.	Found
C_6H_5 -	$C_{15}H_{12}N_2S_2$	160	65	C, 60.00	59.72
				H, 04.00	04.30
p-$CH_3C_6H_4$ -	$C_{16}H_{14}N_2S_2$	158	62	C, 61.14	61.18
				H, 04.45	04.52
p-ClC_6H_4 -	$C_{15}H_{11}N_2S_2Cl$	240	65	C, 53.81	53.63
				H, 03.28	03.30
p-$MeOC_6H_4$ -	$C_{16}H_{14}N_2S_2O$	168	52	C, 58.18	58.61
				H, 04.24	04.16
p-$EtOC_6H_4$ -	$C_{17}H_{16}N_2S_2O$	185	59	C, 59.83	59.59
				H, 04.65	04.58

(ii) *Oxidation of N-arylthiocarbamoyl-p-methoxythiobenzamides* (III) *with bromine in dilute ethanol* : N-Arylthiocarbamoyl-*p*-methoxythiobenzamides (III) were oxidised with bromine in dilute ethanol. Addition of ether gave the respective hydrobromides, which on basification with ammonia afforded the free bases (IV). These were crystallised from ethanol

and were found to be identical with the respective 3-arylimino-5-*p*-methoxyphenyl-1,2,4-dithiazoles (Table 2). The identity was confirmed from undepressed m.m.p. and superimposable ir spectra.

*N-Arylthiocarbamoyl-*p*-methoxythiobenzamides* (III):

(i) *Reductive debenzylation of S-benzyliso-N-arylthiocarbamoyl-*p*-methoxythiobenzamides* (II): The reductive debenzylation of S-benzyliso-N-arylthiocarbamoyl-*p*-methoxythiobenzamides (II) was carried out by dissolving these in a mixture of pyridine-triethylamine (1 : 6) and passing a stream of dry hydrogen sulphide for 4 hr. The reaction mixtures, on pouring over crushed ice and acidification with dilute hydrochloric acid, afforded the related N-arylthiocarbamoyl-*p*-methoxythiobenzamides (III) which were filtered and crystallised from ethanol. The results are recorded in Table 3.

TABLE 3—N-ARYLTHIOCARBAMOYL-*p*-METHOXYTHIOBENZAMIDES (III)

Ar	Molecular formula	m p °C	Yield (%)	Analysis Calcd	Analysis Found
C_6H_5–	$C_{15}H_{14}N_2S_2$	150	74	C, 59 60	60 13
				H 04 63	04 37
p-$H_3CC_6H_4$–	$C_{16}H_{16}N_2S_2$	115	75	C, 60 75	60 47
				H 05 06	04 89
p-ClC_6H_4–	$C_{15}H_{13}N_2S_2Cl$	180	69	C, 53.49	53 53
				H 03.86	03 89
p-$MeOC_6H_4$–	$C_{16}H_{16}N_2S_2O$	165	63	C, 57 83	57 85
				H, 04 81	04 97
p-$EtOC_6H_4$–	$C_{17}H_{18}N_2S_2O$	170	68	C, 58 95	59 02
				H, 05 20	05 31

(ii) *Reduction of 3-arylimino-5-*p*-methoxyphenyl-1, 2, 4-dithiazoles* (IV) *with hydrogen sulphide in pyridine-triethylamine solution*: The related dithiazoles (IV) were dissolved in a mixture of pyridine-triethylamine and were reduced by passing a stream of dry hydrogen sulphide for about 2 hr. The expected N-arylthiocarbamoyl-*p*-methoxythiobenzamides (III) were obtained on pouring the reaction mixture over crushed ice followed by acidification with dilute hydrochloric acid, which were crystallised from ethanol. The identity of each product was established by m.m.p. with authentic samples obtained by the conventional reduction of S-benzyliso-N-arylthiocarbamoyl-*p*-methoxythiobenzamides and also by identical ir spectra.

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Synthesis of Substituted Thiazolo[3,2-*a*]quinazolines

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1,2-Dihydro-5H-thiazolo[3,2-*a*]quinazolin-5-ones with carboxy, carbmethoxy or carbethoxy group in position 2 (IX) have been synthesised by the condensation of ethylanthranilatethiocyanate (I) as well as 2-mercapto-4-ketotetrahydroquinazoline (III) with α,β-dibromopropionic acid or its esters (IV). The products by both the routes have been found to be identical. The structure has been established on the basis of analysis and pmr of one of the compounds.

SOME work has been reported[1-12] on the synthesis of thiazolo-quinazolines. We wish to report the synthesis of some new thiazolo[3,2-*a*]quinazolines with carboxy, carbmethoxy or carbethoxy group in position 2 (IX). These have been synthesised by the condensation of ethylanthranilatethiocyanate (I) or 2-mercapto-4-ketotetrahydroquinazoline (III) with α,β-dibromopropionic acid or its methyl or ethyl esters (IV).

It was reported earlier[13] that the amine thiocyanate (I) changes to the thiourea of the amine (II) on heating and since, in this case, there is formation of 2-thio-4-ketotetrahydroquinazoline (III), 2-carbethoxyphenylthiourea (II) could be the intermediate. The intermediate thiourea (II), formed *in situ*, might react with vicinal dihalo compounds (IV) leading to the formation of linear product VIII or angular product IX or both. But we could isolate one compound only, as evident by tlc, to which we have assigned structure IX on the basis of pmr.

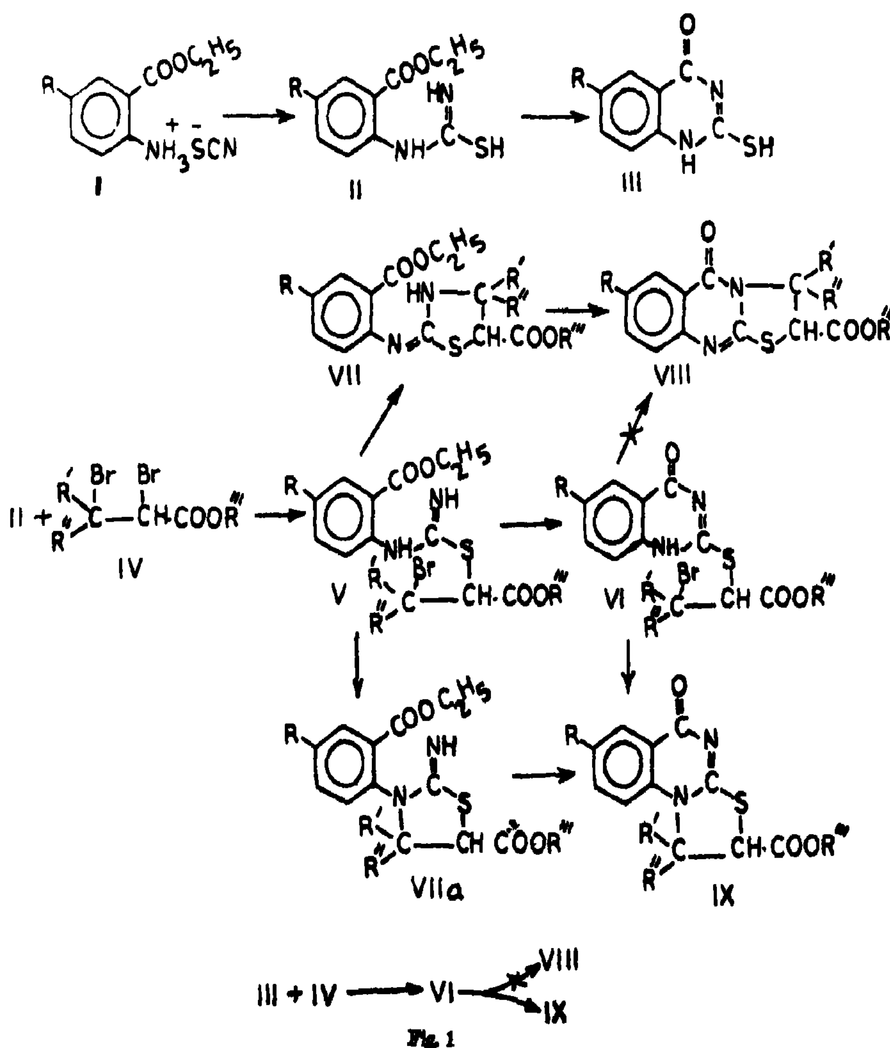


Fig. 1

IXc which has a thiazole ring with carboxy and dimethyl groups like that of penicillin showed in its PMR* (in DMSO-d_6) a multiplet (4H) at 7.3-8.2 assignable to four aromatic protons. It also showed a singlet (3H) at 2.6 due to three methyl protons (R′). Another singlet (4H) appeared at 3.45 which could be considered as due to overlapping of signals of three methyl protons (R″) with one methine proton at position 2. This down-field shift of three methyl protons may be attributed to its vicinity to the aromatic ring. The carboxylic acid proton appeared as a broad signal at 12.6.

Experimental

Melting points were taken in open glass capillaries in paraffin liquid bath and are uncorrected. PMR was recorded on Varian EM-390 90MHz spectrometer using TMS as the internal reference.

2-Carbmethoxy-1,2-dihydro-5H-thiazolo [3,2-a] *quinazoline-5-one* (IX*a*, *R = R′ = R″ = H*; *R‴ = CH₃*) :

Method A · Ethylanthranilatethiocyanate (1.5 g) was mixed with methyl α,β-dibromopropionate (15 g) and the contents were heated in an oil bath at 120°. After half an hour, a clear solution was obtained, followed by separation of a solid. It was cooled, the product collected under suction and identified to be 2-thio-4-ketotetrahydroquinazoline (m.p., m m p., R_f value and superimposable ir spectrum with an authentic sample).

In another experiment, the temperature was maintained at 120° for half an hour and then gradually raised to 150°. In this case, the quantity of 2-mercapto-4-ketotetrahydroquinazoline went on increasing with time for 2 hr after which it went on decreasing with the simultaneous separation of a solid as evident by tlc. The heating was continued for 3 hr more to complete the reaction. The reaction mixture was cooled and the product collected under suction. It was crystallised from ethanol into white needles, m.p. 254°, yield 61%.

Method B : 2-Mercapto-4-ketotetrahydroquinazoline (1.5 g) was mixed with methyl α β-dibromopropionate (15 g) and the contents heated in an oil bath at 150° for 2 hr. After cooling, the product was collected under suction. Crystallisation from ethanol gave white needles, m.p. 254, yield 80%. The product was found to be the same as in 'A'.

The other compounds of the series except IXc were also prepared by method B. The data regarding the yields of these compounds, their m p., solvent for crystallisation and analytical results are tabulated in Table 1.

*Chemical shifts given in this paper are in δ(ppm).

TABLE 1—THIAZOLO[3,2-a]QUINAZOLIN-5-ONES

Compound	R	R′	R″	R‴	Yield %	m.p. °C	M.F.
a	H	H	H	CH_3-	80	254	$C_{12}H_{11}BrN_2O_3S$
b	H	H	H	C_2H_5-	77	248	$C_{13}H_{13}BrN_2O_3S$
c	H	CH_3-	CH_3-	H	60	283	$C_{13}H_{12}N_2O_3S$
d	H	H	C_6H_5-	C_2H_5-	38	205	$C_{19}H_{16}N_2O_3S$
e	CH_3-	H	H	CH_3-	61	272	$C_{13}H_{13}BrN_2O_3S$
f	CH_3-	H	H	C_2H_5-	48	274	$C_{14}H_{15}BrN_2O_3S$

Compound a, b, c, e and f were crystallised from ethanol while compound d was crystallised from glacial acetic acid All the compounds except c and d were isolated in the form of their hydrobromides.

Satisfactory elemental analysis for the above componnds were obtained

2-Carbethoxy-1,2-dihydro-1,1-dimethyl-5H-thiazolo [3,2-a] *quinazoline-5-one* (IX*c*) : A solution of α,β-dibromo-β,β-dimethylpropionic acid (1.30 g ; 0.05 mol) in ethanol (15 ml) was mixed with a solution of 2-mercapto-4-ketotetrahydroquinazoline (0.90 g ; 0 05 mol) in 100 ml of the same solvent. The contents were refluxed on a steam bath for 4 hr, cooled and the product collected under suction.

The mother liquor was concentrated when a further crop of the product was obtained. Both the compounds were crystallised separately from ethanol and were found to be identical.

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Heterocyclic Quinones—Part III : Synthesis of Dialkylbenzodipyrrocolinequinones

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A series of unsymmetrical dialkylbenzodipyrrocolinequinones has been synthesised by condensing chloranil with alkylpyridines giving both *trans* and *cis* forms of the compounds as evidenced through their elemental and spectral analysis.

IN our previous communications[1-3] we described the synthesis of disubstituted benzo-dibenz-pyrrocolinequinones. A persual of literature reveals that no work has been done on the reaction of chloranil with alkylpyridines. A reaction of 2,3-dichloro-1,4-naphthoquinone with ∝-picoline has been reported[4]. We now report the synthesis of some new dialkylbenzodipyrrocolinequinones (*trans* and *cis* forms) obtained by the condensation of chloranil with alkylpyridines (i.e. ∝-picoline, 2,4-lutidine, 2,6-lutidine). In the case of quinaldine and collidine no products could be isolated. This may be ascribed to steric effect.

The *trans* and *cis* structure of these quinones has been established on the basis of colour reaction with conc. H_2SO_4[4] The compounds of *trans* configuration gave violet to blue coloured solution whereas those of *cis* configuration gave olive green to green solution with conc. H_2SO_4. The ir spectra of these compounds showed characteristic bands at 1675 (C=O), 1315 cm^{-1} (C-N).

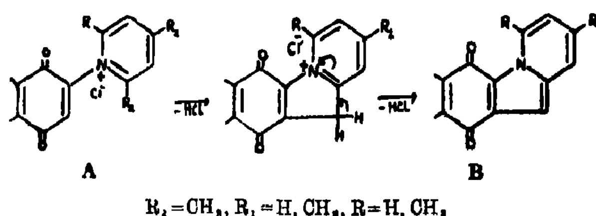
The uv spectra of both *trans* and *cis* structures showed the presence of three prominent absorption maxima. As expected, the *trans* isomers show absorption at longer wavelengths as compared to the corresponding *cis* isomers (Table 1).

Experimental

All melting points were determined on a Kofler instrument and are uncorrected. UV absorption spectra of these compounds were recorded on a Beckman spectrophotometer, Model DU-2, using 1 cm path length quartz cells. IR spectra were determined on a Perkin-Elmer Infracord model-577 using KBr disc. The procedure for the preparation of substituted benzo-dipyrrocolinequinones is described below.

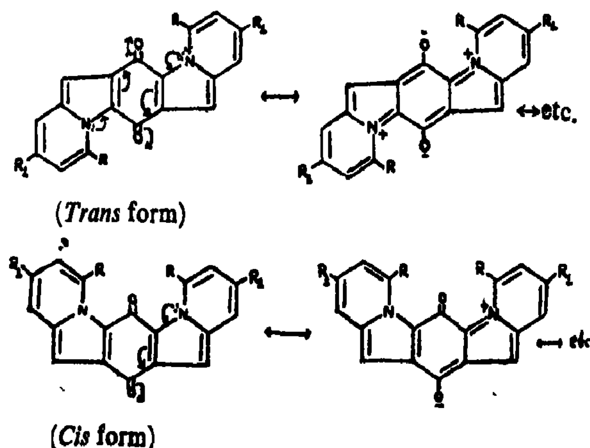
Chloranil (1 mol) was taken in 50 ml DMF. Alkyl pyridine (2 mol) was added slowly to this in a period of 10 min. The reaction mixture was boiled under reflux on a water bath for 4 hr and then the solution was allowed to stand overnight. The product (*trans* form) separated, was filtered, washed several times with small portions of ethanol, then with ether and dried. The filtrate was concentrated and water was added to it till the solution was turbid. The product (*cis* form) was obtained. It was filtered and washed with hot water, ethanol, ether and dried. Both forms of the compounds were recrystallised from desired solvent. The analysis, m.p., etc. are given in Table 1.

Mechanism : The reaction sequence for the formation of these compounds may be explained as : (1) quaternisation of the alkylpyridine with chloranil to give A [rendering the methyl group (R_2) more reactive], (2) A now gets cyclized to B by the elimination of HCl as shown below.



$R_1=CH_3, R_2=H, CH_3, R=H, CH_3$

The *trans* structures provide larger scope for electronic excitation as compared to the *cis* structures as shown below which explains their absorption at longer wavelengths.



(*Trans* form)

(*Cis* form)

TABLE 1—SUBSTITUTED BENZO-DIPYRROCOLINE QUINONES*

Sl. No.	R	R_1	Molecular formula	Form of compd	Recrystallization solvent	% Analysis Calcd	% Analysis Found	UV spectra DMF λ_{max} nm	UV spectra DMF log ε
1	H	H	$C_{18}H_{10}N_2O_2$	*Cis*	Acetone	C, 75.5	75.2	329	3.87
						H 3.4	3.3	357	4.05
						N, 9.7	9.5	475	4.10
				Trans	Benzene	C, 75.5	75.4	335	3.91
						H, 3.4	3.4	351	4.15
						N, 9.4	9.6	581	4.25
2	H	CH_3	$C_{20}H_{14}N_2O_2$	*Cis*	Acetone +	C, 76.4	76.4	324	3.96
						H, 4.4	4.2	350	4.07
					Alcohol	N, 8.9	8.8	467	4.15
				Trans	Benzene	C, 76.4	76.2	330	3.87
						H, 4.4	4.4	347	4.10
						N, 8.9	8.9	575	4.21
3.	CH_3	H	$C_{20}H_{14}N_2O_2$	*Cis*	Acetone	C, 76.4	76.8	320	3.85
						H, 4.4	4.4	366	4.15
						N, 8.9	8.7	463	4.13
				Trans	Benzene	C 76.4	76.4	339	3.90
						H, 4.4	4.1	355	4.21
						N 8.9	8.6	587	4.49

* Both the isomers do not melt upto 330°.

Acknowledgement

Thanks of the authors are due to Prof. R. C. Kapoor, Head of Chemistry Department for necessary facilities and to the U. G. C., New Delhi, for the award of a Junior Research Fellowship to one of them (R. P. S.).

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On 1,3,5-Triazines. Part—II : Synthesis of 2,4-Dithio-3,5-Diaryl-6-Phenylimino-Hexahydro-1,3,5-Triazines and 2,6-Dithio-3,5-Diaryl-4-Phenylimino-Hexahydro-1,3,5-Triazines

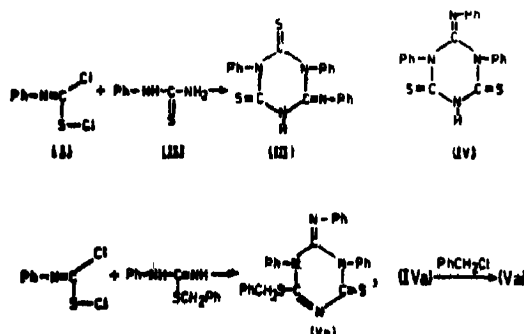
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New synthetic procedures are reported for the preparation of 2,4-dithio-3,5-diaryl-6-phenylimino-hexahydro-1,3,5-triazines (III) and 2,6-dithio-3,5-diaryl-4-phenylimino-hexahydro-1,3,5-triazines (IV), respectively. The formation of 1,3,5-triazines, viz. IIIa and IVa, incidentally has settled the structural problem of the reaction product of N-phenyl-S-chloro isothiocarbamoyl chloride and phenyl thiocarbamide.

INTERACTION of N-phenyl-S-chloro isothiocarbamoyl chloride (I)[1] and phenyl thiocarbamide (II) afforded a product[2], m.p 218°. On reaction with benzyl chloride followed by basification, 2-mercaptobenzyl derivative, m p 136°, has been isolated. Earlier, a structure 2,4-dithio-3,5-diphenyl-6-phenylimino-hexahydro-1,3,5-triazine (IIIa) was assigned to this product. Afterwards, a new structure 2,6-dithio-3,5-diphenyl-4-phenylimino-hexahydro-1,3,5-triazine (IVa)[3] has been suggested to this reaction product, on the basis of the formation of identical 2-mercapto benzyl (free base) derivative[3], m.p. 136°, by the interaction of I and S-benzyl phenyl isothiocarbamide.



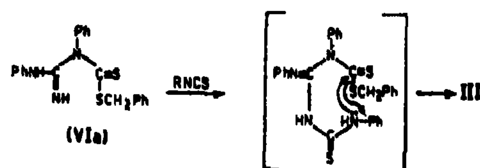
We have now successfully synthesized IIIa and IVa independently, former by the interaction of benzyl phenylamidino phenyldithiocarbamate (VIa) and phenyl isothiocyanate (VII) and the latter by the interaction of 1,5-diphenyl-2,4-dithiobiuret (VIIIa) and phenyl isocyanodichloride (IX)[5]. These two syntheses have finally settled the structural problem of the reaction product of phenyl thiocarbamide and N-phenyl-S-chloro isothiocarbamoyl chloride[3]. The present communication is the record of these studies.

(I) *Synthesis of 2,4-dithio-3,5-diphenyl-6-phenylimino-hexahydro-1,3,5-triazine* (IIIa) *:* Benzyl phenylamidino phenyldithiocarbamate[4] on reaction with phenyl isothiocyanate at 140-150° afforded a yellow semi-solid, which on several triturations with petroleum ether followed by ethanol was converted into a solid, crystallized from ethanol, m.p. 255°. The product has been assigned structure IIIa on the basis of the following facts.

It was non-desulphurizable when boiled with alkaline plumbite solution. On pyrolysis, smell of phenyl isothiocyanate was quite perceptible. On mixing with the product, m.p. 218°[3] it depressed its m p. The ir spectrum of the product clearly indicated the presence of $\nu_{C=N}$ (1675 cm^{-1}), $\nu_{C=S}$ (1070 cm^{-1}) and ν_{-NH} (3225 cm^{-1}) stretching frequencies.

The same reaction of benzyl phenylamidino phenyldithiocarbamate, when extended to *p*-tolyl isothiocyanate, yielded the related 1,3,5-triazine (IIIb), m.p. 216°.

The reaction may be stated as follows :



where R= (a) phenyl and (b) *p*-tolyl

(II) *Synthesis of 2,6-dithio-3,5-diphenyl-4-phenylimino-hexahydro-1,3,5-triazine* (IVa) *:* 1,5-Diphenyl-2,4-dithiobiuret[5] on reaction with phenyl isocyanodichloride (IX)[6] in boiling benzene offered a dark yellow unstable solid, m.p. 65° (d), which on trituration with petroleum ether followed by ethanol isomerized into a white solid crystallized from chlorobenzene, m.p. 220°. It has been assigned the structure IVa on the basis of the following chemical transformations and ir spectral data.

The product was soluble in alkali and could be reprecipitated unchanged on acidification. This indicated the presence of a thiol (–SH). It was

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TABLE 1—2,6-DIARYLIMINO-4-PHENYLIMINO-DIHYDRO-1,3,5-DITHIAZINE (X) AND 2,6-DITHIO-3,5-DIARYL-4-PHENYLIMINO-HEXAHYDRO-1,3,5-TRIAZINE (IV)

1,5-Diaryl-2,4-dithiobiuret (0.02 mol) and phenyl isocyanodichloride (4 g ; >0.02 mol) in dry boiling benzene for 3-5 hr.

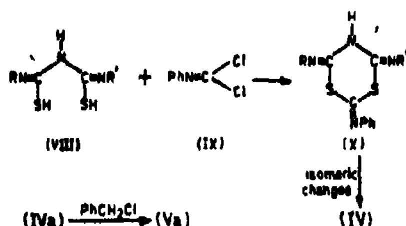
Sl. No.	1,5-Diaryl-2,4-dithiobiuret g	(VIII)	-1,3,5-dithiazine(unstable) (X)* Yield %	m p °C	Analysis % Found	Reqd	-1,3,5-triazine (IV)** Yield %	Nature of crystals and solvent used	m.p. °C	Analysis% Found	Reqd.
1.	1,5-Diphenyl- 5.7	VIIIa	58 4	65(d)	N, 13.91 S, 15.58 Eq wt. 414 6	13.22 15.11 424.5	55.8	White, amorphous, chlorobenzene/ acetic acid	220	N, 14.24 S, 16.16	14.43 16.49
2.	1-*m*-Tolyl-5-phenyl- 6.0	VIIIb	53.6	71(d)	13.21 15.04 425.3	12.80 14.60 438 5	48 9	—do—	215	13.75 15 80	13.98 15.92
3.	1-*p*-Tolyl-5-phenyl- 6.0	VIIIc	61 5	75(d)	13 18 15 00 419.8	12 80 14.60 438.5	46 3	—do—	219	13 82 15 82	13 93 15 92
4.	1-*m*-Chlorophenyl-5-phenyl- 6.4	VIIId	54 5	69(d)	12.81 14.32 448.5	12.20 13 94 459 0	50 0	—do—	216	13.01 14 85	13.25 15.14
5.	1-*p*-Chlorophenyl-5-phenyl- 6 4	VIIIe	54 4	72(d)	12 75 14.26 448 4	12.20 13 94 459.0	52.0	—do—	218	13.11 14 90	13.25 15.14

* Nature of crystals : Dark yellow in colour in all cases
** Satisfactory C and H analyses have been obtained in all cases

unreactive towards hot ethanolic ammoniacal hydrogen sulphide and non-desulphurisable when boiled with alkaline plumbite solution. On pyrolysis, the smell of phenyl isothiocyanate was quite perceptible. It was identical with the reaction product of N-phenyl-S-chloro isothiocarbamoyl chloride and phenyl thiocarbamide[8] on the basis of m.m.p. On reaction with benzyl chloride (1 : 1), it afforded a hydrochloride of mercapto benzyl derivative, m p. 172°, thus indicating the presence of $-NH-C=S$ group, which on basification gave a free base, m p. 136°. This compound was found indentical with the reaction product of I and S-benzyl phenyl isothiocarbamide, m.p. 136°[8], on the basis of m.m.p.

The ir spectrum of the product clearly indicated the presence of ν_{-NH} (3180 cm^{-1}), $\nu_{C=N}$ (1630 cm^{-1}), $\nu_{C=S}$ (1015 cm^{-1}) bands. Two more bands at 1550 cm^{-1} and 750 cm^{-1} suggested the isotriazine ring[7,8]. The bands due to $-SH$ were not located, probably because of its weak nature.

This synthetic procedure could be used to prepare several other 1,3,5-triazines (IVb-IVe) in excellent yields (Table 1). All these products were white in colour and amorphous in nature.



where, (a) R=R′=phenyl;
(b) R=*m*-tolyl, R′=phenyl,
(c) R=*p*-tolyl, R′=phenyl;
(d) R=*m*-chlorophenyl, R′=phenyl;
(e) R=*p*-chlorophenyl, R′=phenyl.

Experimental

The required benzyl phenylamidino phenyldithiocarbamate[4] has been prepared by the isomeric conversion of monosulphide salt obtained by the interaction of S-benzyl phenyl dithiocarbamate[4] and phenyl amidinechloride[9]. Aryl isothiocyanates (VII) were prepared by the oxidative decomposition of the related ammonium salts of dithiocarbamic acids with lead nitrate. 1,5-Diaryl-2,4-dithiobiurets (VIII)[4] have been prepared by the interaction of S-benzyl isothiocarbamide and aryl isothiocyanate followed by thiohydrolysis of the related isodithiobiurets. The required phenyl isocyanodichloride (IX)[4] has been prepared by the interaction of excess chlorine and phenyl isothiocyanate.

Formation of 2,4-dithio-3,5-diphenyl-6-phenylimino-hexahydro-1,3,5-triazine (IIIa) : A mixture of benzyl-N-phenylamidino phenyldithiocarbamate (VIa) (1 g) and phenyl isothiocyanate (1 ml) was heated at 140-150° for 4 hr. The resultant yellow semi-solid on trituration several times with petroleum ether followed by little ethanol, gave a pale yellow solid (1.8 g) crystallized from chlorobenzene, m.p. 255° (Found : N, 14.16 ; S, 16.29. $C_{21}H_{16}N_4S_2$ requires N, 14.43 ; S, 16.49%).

Formation of 2,6-dithio-3,5-diphenyl-4-phenylimino-hexahydro-1,3,5-triazine (IVa) : To a suspension of 1,5-diphenyl-2,4-dithiobiuret (5.7 g ; 0.02 mol) in benzene (50 ml), phenyl isocyanodichloride (4 g ; > 0.02 mol) was added and refluxed for 3-5 hr. Evolution of hydrogen chloride was noticed. On washing the resultant semi-solid several times with benzene followed by petroleum ether, an acidic unstable dark yellow solid (5.2 g), m.p. 65°(d) (Xa) was isolated (Found : N, 13.91 ; S, 15.53 ; Eq. wt.

414.6. $C_{21}H_{18}N_4S_2$, HCl requires N, 13.22; S, 15.11%; Eq. wt. 424.5). On reaction with aqueous picric acid this afforded a picrate crystallizable from ethanol, m.p. 240° (Found: N, 16.15; S, 10.24. $C_{21}H_{18}N_4S_2$, $C_6H_3N_3O_7$ requires N, 15.91; S, 10.39%).

This on treatment with ethanol isomerised into a solid (2.9 g), crystallized from chlorobenzene, m.p. 220° (Found: N, 14.24; S, 16.16. $C_{21}H_{18}N_4S_2$ requires N, 14.43; S, 16.49%). This was identified as 2,6-dithio-3,5-diphenyl-4-phenylimino-hexahydro-1,3,5-triazine (IVa).

When the reaction of phenyl isocyanodichloride was extended to other 1,5-diaryl-2,4-dithiobiurets (VIIIb-VIIIe), the corresponding 1,3,5-dithiazines (Xb-Xe) were isolated. Because of their unstable nature, these could not be purified. All these have been successfully isomerised into the corresponding 1,3,5-triazines (IVb-IVe) on prolonged treatment with ethanol (Table 1).

Acknowledgement

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Addition of Sulphene to Substituted Benzalanilines

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1,4-Benzothiazines have been synthesized by the addition of sulphene, prepared *in situ* by the action of triethylamine on methane sulphonyl chloride, to 4-chlorobenzalanilines, 4-methoxybenzalanilines and 3,4-dimethoxybenzalanilines, through a novel rearrangement of the anticipated (2+2) cycloadducts.

IN an earlier communication we reported the reaction of sulphene with benzalanilines[1]. This paper describes the reaction of sulphene with C-phenylsubstituted benzalanilines e g., 4-chlorobenzalanilines, 4-methoxybenzalanilines and 3,4-dimethoxybenzalanilines.

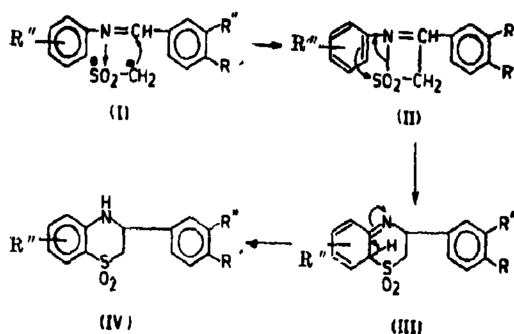
Addition of sulphene to substituted benzalanilines under the reaction conditions described earlier[1] either does not take place at all or results in poor yields. This is perhaps due to the poor solubility of these benzalanilines in solvent ether This forced the authors to modify the reaction conditions.

Under modified conditions the reaction has been carried out by adding equimolar amounts of methane sulphonyl chloride and triethylamine simultaneously through dropping funnels to a constantly stirred benzene solution of the substituted benzalaniline, taken in a three necked flask, over 0.5 hr. Further stirring, filtration of triethylammonium chloride and removal of benzene *in vacuo* yields the crude product which is recrystallized from ethanol or methanol.

Moreover, it has also been observed that under the modified reaction conditions yields of the cycloadducts of sulphene and benzalanilines[1,2] are increased.

4-Chlorobenzalanilines, 4-methoxybenzalanilines and 3-4-dimethoxybenzalanilines react with sulphene, generated *in situ* by the reaction of triethylamine on methane sulphonyl chloride to give 1,4-benzothiazines. These products are obtained through a novel rearrangement of the anticipated (2+2) cycloadducts (Scheme 1).

These products are identified and confirmed as 1,4-benzothiazines on the basis of elemental analysis and spectral studies. The infrared spectra of these products show sharp bands at about 3100 cm^{-1} thereby indicating the presence of an associated NH group. The presence of this band suggests the



Scheme 1

migration of the sulphone group from the nitrogen atom of the aniline moiety to the *ortho*-carbon of the N-phenyl ring, followed by a protonic shift from the ring to the nitrogen atom under acidic conditions (Scheme 1), thus rearranging the four membered 2-thiazetidine ring into a six membered 1,4-benzothiazine ring. Such migrations have already been reported in the case of sulphene adducts of nitrones[3]. The infrared spectra also show bands at 1300-1350 cm^{-1} and 1140-1160 cm^{-1}, indicating the presence of the sulphone group.

NMR spectral measurements also support the 1,4-benzothiazine structure assigned to these compounds The nmr spectrum of the cycloadduct (IV) ($R' = R'' = OCH_3$, $R''' = Cl$) shows one (NH) proton as a singlet at 7.2 τ, two methylene protons as a doublet at 2.8 τ, one (CH) proton at 6.6 τ and aromatic protons as a multiplet between 2.5 to 2.8 τ.

The adducts obtained by the addition of sulphene to 4-chlorobenzalanilines, 4-methoxybenzalanilines and 3,4-dimethoxybenzalanilines are recorded in Table 1.

Experimental

The following general procedure was adopted. A solution of 0.02 mole of 4-chlorobenzalaniline in

TABLE 1—1,4-BENZOTHIAZINES

Sl. No.	Substituent in N-phenyl R	Substituents in C-phenyl R	R	Yield %	m.p.* °C
1.	H	H	Cl	75	140
2.	p-CH_3	H	Cl	72	124
3.	p-OCH_3	H	Cl	70	120
4.	p-Cl	H	Cl	70	109
5.	p-I	H	Cl	60	143
6.	H	H	OCH_3	72	85
7.	p-CH_3	H	OCH_3	72	74
8.	p-OCH_3	H	OCH_3	70	144
9.	p-Cl	H	OCH_3	75	195
10.	p-NO_2	H	OCH_3	60	183
11.	H	OCH_3	OCH_3	70	99
12	p-OCH_3	OCH_3	OCH_3	70	105
13.	p-OC_2H_5	OCH_3	OCH_3	68	197
14.	p-I	OCH_3	OCH_3	55	184

* All melting points are uncorrected.
The compounds gave consistent nitrogen and sulphur analysis.

150 ml of benzene was taken in a 500 ml three necked flask equipped with two dropping funnels. To the mechanically stirred solution, equivalent amounts of methane sulphonyl chloride and triethylamine, each in 30 ml of benzene, were added simultaneously over a period of 0.5 hr. During the course of the reaction triethylammonium chloride precipitated out and an intense colour also developed. The reaction mixture was stirred for about 10 hr after the addition was complete. The triethylammonium chloride was filtered out. The filtrate was evaporated *in vacuo* yielding highly coloured semi-solid which was induced to crystallize by adding small amounts of ethanol. Cooling and filtration usually gave almost pure product. Recrystallization from ethanol gave pure adduct in 75% yield, m.p. 140°.

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Synthesis and Biological Activity of Some New 2-(N-Substituted Carboxamidomethyl Thio)-Naphth[1,2-d]Oxazoles—Part V

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Several 2-(N-aryl carboxamidomethyl thio)naphth [1,2-d]oxazoles (II and III) and 2-(N-p-aryl sulphonanilido carboxamidomethyl thio)naphth[1,2-d]oxazoles (IV and V) have been prepared via the interaction of naphth[1,2-d]oxazole-2-thiols with different N-aryl chloroacetamides and/or N-(p-aryl sulphonanilido)chloroacetamides respectively. Moreover, oxidation of some 2-(N-aryl carboxamidomethyl thio)naphth[1,2-d]oxazoles (IIa, d, e, i and o) to the corresponding sulphones (Va-Ve) were undertaken. The biological activities of the compounds (IIa-III and IIIa-IIII) were screened against some bacteria and fungi.

BASIC acetamides, in which amido-H has been substituted with aromatic[1] or heterocyclic[2] moieties have been prepared in large numbers as potential local anaesthetics. Several basic N-(2-thienyl/furfuryl) acetamides have been patented as analgesic and antispasmodics[3]. Further, condensed oxazole derivatives possess valuable biological properties[4-8]. Recently, some biologically active naphthoxazole sulphonamides[6], sulphonic esters[8], thiosulphonic esters[8], thiols[9], alkylmercapto-[9], arylmercapto-[10] and acridinomercapto-[6] were synthesised in our laboratories.

The remarkable biological activities of these naphthoxazoles motivated us to synthesise some new N-substituted carboxamidomethyl thio naphth-[1, 2-d]oxazoles (II-V) and to evaluate their antimicrobial activities.

Experimental

Melting points reported are uncorrected. IR spectra (KBr) were recorded on a Pye-Unicam SP 200 G spectrophotometer. UV spectra in spec. pure ethanol were taken on a Pye-Unicam SP 8000 ultraviolet spectrophotometer. NMR spectra in DMSO recorded on a Varian, 60 MHZ NMR. The time allowed for the completion of the reaction, and the purity of the prepared compounds were controlled by tlc.

Reaction of naphth[1,2-d]oxazole-2-thiols[9] *(I) with N-aryl-2-chloroacetamides :* Formation of 2-(N-substituted carboxamidomethyl thio) naphth[1,2-d]-oxazoles (II-V). Naphth[1,2-d]oxazole-2-thiol[9] (0.001 mole) was dissolved in ethanol (20 ml) in the presence of an equivalent amount of KOH and the appropriate N-aryl chloroacetamide (0.001 mole) or N-(p-aryl sulphonanilido)chloroacetamide was added to it. The reaction mixture was refluxed for about 30 min, concentrated and cooled, when a mixture of the crude compounds II, III or/and IV, V and potassium chloride was precipitated.

TABLE 1—PHYSICAL DATA OF COMPOUNDS II, III AND V

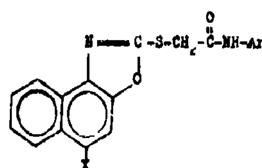
Compound*	m.p. °C
IIa	144-45
IIb	155-56
IIc	210-11
IId	176-77
IIe	145-46
IIf	183-84
IIg	160-61
IIh	140-41
IIi	234-35
IIk	174-75
IIl	139-40
IIm	124-25
IIn	179-80
IIo	158-59
IIIa	>360
IIIb	250-51
IIIc	312-13
IIId	266-67
IIIe	309-10
IIIf	>360
IIIg	327-28
IIIh	>360
IIIi	>360
IIIj	>360
IIIk	356-57
IIIl	>360
IIIn	>360
IIIo	323-24
IVa	182-83
IVb	>360
Va	198-99
Vb	244-45
VIIa	245-47d
VIIb	145-47
VIIc	185-88d
VIId	205-10d
VIIe	160-61

* Compounds IIa-o, IIIa-o, IVa-b, Va-b and Va-e were obtained in 70-80, 73-90, 75, 60 and 50-65% yields, respectively.
All the compounds gave consistent C, H, N and S analysis.

Acidification with acetic acid, filtration, removal of potassium chloride by water washing and recrystallization from ethanol gave II or/and III (Table 1).

2-Naphth[1, 2-d]oxazole thioacetic acid (VI) was prepared by the above method, through the interaction of naphth[1, 2-d]oxazole thiol (Ia) and monochloroacetic acid in ethanol and KOH. The compound (VI) was recrystallized from ethanol in about 70% yield, m p. 205°, R_f 0.82 (benzene and ethylacetate mixture 9 : 1) (Found : C, 60.06 ; H, 3.39 ; N, 5.34 ; S, 12.48. Calcd for $C_{13}H_9NO_3S$; C, 60.23 ; H, 3.47 ; N, 5.40 ; S, 12.35%).

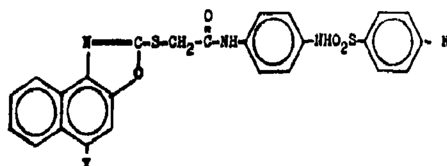
Reaction of 2-naphth[1, 2-d]oxazole thioacetic acid (VI) with aromatic amines · A mixture of compound VI (0.001 mole), aromatic amine (0.001 mole) and N-ethoxycarbonyl-2-ethoxy-1, 2-dihydroquinoline[11] (EEDQ) (0.001 mole) was dissolved in DMF (4 ml). The reaction mixture was kept at room temperature for 24 hr, then seeded. The product was recrystallized from ethanol into compounds (IIa-h).



(II X=H)
(III X=SO_3H)

	Ar		Ar
a	C_6H_5	i,	C_6H_4-COOH-*p*
b	C_6H_4-Cl-*p*	j,	C_6H_4-OH-*p*
c,	$C_6H_4-CH_3$-*p*	k,	$C_6H_4-CH_3$-*o*
d,	C_6H_4-Br-*p*	l	C_6H_4-Cl-*o*
e	$C_6H_4-OCH_3$-*p*	m	$C_6H_4-NO_2$-*o*
f,	$C_6H_4-NO_2$-*p*	n,	$C_{10}H_7$-α
g,	$CH_2-C_6H_5$	o,	$C_{10}H_7$-β

Oxidation of 2-(N-aryl carboxamidomethyl thio)-naphth[1,2-d]oxazoles (IIa, IId, IIe, IIi and IIo) *with hydrogen peroxide*[10,14] · *Formation of sulphones* (Va-d) *:* To a solution of thioether (IIa, IId, IIe, IIi or IIo) (0.005 mole) in acetic acid (5 ml) was added hydrogen peroxide [5 ml, 30% (w/v)], the reaction mixture warmed on a water-bath for 1 hr, cooled and diluted with water. The separated sulphone (Va, Vb, Vc, Vd or Ve) was recrystallized from ethanol, yield (50-65%) (Table 1).



(IV, X=H)
(V ; X=SO_3H)

R

a ; H
b , CH_3

Results and Discussion

In the present investigation, a series of new substituted carboxamido methyl thio-naphth[1,2-d] oxazoles (II-V) has been prepared (c.f. Table 1). These compounds are stable as indicated from their resistance to boiling water, hot 0.1 *N* HCl and 0.1 *N* NaOH solution and can be recrystallized from organic solvents. Naphtoxazole sulphonic acid derivatives, III and V, show an outstanding violet fluorescence in organic solvents (methanol, ethanol, butanol and ethylene glycol).

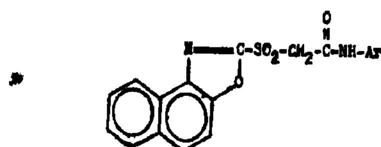
Compounds II-V have been identified by a combination of their elemental analysis and spectral data. The ir spectra showing absorption bands at 3430-3350 cm^{-1} (NH amide)[12], 1660 cm^{-1} (C=O amide)[12], 1630-1610 cm^{-1}, 1610-1580 and 1570-1540 cm^{-1}. The last three bands were assigned to the vibrations arising from the heterocyclic oxazole system[8,9,13]. Substituted 2-(N-aryl carboxamidomethyl thio)naphth[1,2-d]oxazoles (IIb-IIm and IIIa-IIIo) showed, in addition, the bands characteristic of the substitutent groups, e.g. at 1350 cm^{-1} for the NO_2 group, at 3535 cm^{-1} for the OH group and two vibration bands at 1060 cm^{-1} and 650 cm^{-1} for the sulphonic group[13].

The uv spectra of naphthoxazole compounds (IIa-IIg) showed three λ_{max} at 280-290, 310-315 and 330-340 nm similar to substituted naphthoxazoles[8].

The nmr spectrum of compound (IIa) showed the following signals at $\delta=3.24$ (s, 2H, CH_2) ; $\delta=4.4$ (s, 1H, NH) and $\delta=7.9-7.2$ (m, 11H, aromatic), which are in accordance with its structure.

2-(N-aryl carboxamidomethylthio)naphth[1,2-d]-oxazoles (IIa-IIh) could also be obtained through an alternative route by condensation of 2-naphth-[1, 2-d]oxazole thioacetic acid (VI) with different aromatic amines in the presence of N-ethoxycarbonyl-2-ethoxy-1, 2-dihydroquinoline (EEDQ)[11] as condensing agent and DMF as a solvent.

2-(N-aryl carboxamidomethyl thio)naphth[1,2-d]-oxazoles compounds IIa, IId, IIe, IIi ond IIo were converted by hydrogen peroxide in acetic acid[10,14] to the corresponding sulphones (VIIa-VIIe). Elemental as well as spectroscopic analysis of sulphones (VIIa-VIIe) are in accordance with the suggested structures. The ir spectra show an absorption band at about 1340-1320 cm^{-1} characteristic of the sulphone group[10,13].



VII

	Ar		Ar
a ;	C_6H_5	c ;	$C_6H_4-OCH_3$-*p*
b ;	C_6H_4-Br-*p*	d ,	C_6H_4-COOH-*p*
		e ;	$C_{10}H_7$-β

Antimicrobial activities : The antimicrobial activities of the compounds of the types IIa-IIi, IIIa-IIIi, IVa and Va were tested *in vitro* against bacteria[15], including gram-positive and gram-negative, such as *Staphylococcus albus* and *Bacillus megatherium* and against fungi[16], such as *Aspergillus flavus* and *Penicillium notatum*. The results indicated that most of the compounds (II and III) showed feeble (25%) to moderate (75%) inhibition at a concentration of 20 mg/l.

The compounds more active against *S. albus* are IIa, IIe, IIIa, IIIe and Va, against *B. megatherium* are IIa, IIb, IIIb, IIIe and IIIi, against *A. flavus* are IIe, IIi and IIIi and against *P. notatum* are IIe, IIi, IIIa, IIIb, IIIe, IIIi and Va.

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Studies on Acetamide Derivatives : Preparation and Antimicrobial Activity of 2-α-Arylaminoacetamido/α-Carbamoyl benzylamino/Arylcarbamoylmethylamino-5-o-Nitrophenyl/Benzoylaminomethyl-1,3,4-Thiadiazole

V. H. SHAH, H. H. PATEL and A. R. PARIKH

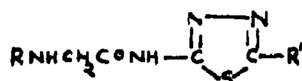
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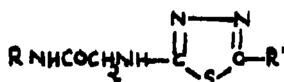
Some new 1,3,4-thiadiazoles having acetamide sidechain at two position have been prepared. The products were screened for antimicrobial activity.

ACETAMIDE derivatives have been found to possess antiarrhythmic[1], antimetastatic[2], psychoneurosis[3], schistosomicidal[4], fungicidal[5], herbicidal[6], pesticidal[7] activities. 1,3,4-Thiadiazole derivatives have been found to possess herbicidal[8], radioprotective[9], antitumor[10], diuretic[11], bacteriostatic[12], cytostatic[13] activities.

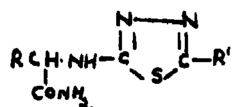
With a view to prepare better therapeutic agent, we undertook the preparation of 2-amino-5-*o*-nitrophenyl- and 2-amino-5-benzoylaminomethyl-1,3,4-thiadiazoles by the cyclisation of *o*-nitrophenyl-3-thiosemicarbazide[14] and benzoylaminomethyl-3-thiosemicarbazide. The products were (i) chloroacetylated and condensed with different amines to give compounds of type (I), (ii) condensed with chloroacetylated amines to give compounds of type (II), and (iii) condensed with different aldehyde-cynohydrin and treated with conc. H_2SO_4 to give compounds of the type (III).



(I)



(II)



(III)

where R = Aryl, R' = *o*-Nitrophenyl/Benzoylaminomethyl

The products were screened for antimicrobial activity.

Experimental

Preparation of 2-amino-5-o-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole : *o*-Nitrophenyl-3-thiosemicarbazide or benzoylaminomethyl-3-thiosemicarbazide (20 g) was treated with conc. H_2SO_4 and poured into cold water and product was isolated; *o*-nitrophenyl derivative, yield 66%; m.p. 233°, reported[14] 234°; benzoylaminomethyl derivative, yield 70%; m.p; 216°. Found. C, 51.25; H, 4.26; N, 23.90; S, 13.65. $C_{10}H_{10}N_4OS$ requires C, 51.28; H, 4.27; N, 23.93; S, 13.67%.

Chloroacetylation of 2-amino-5-o-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole and different amines : The chloroacetylation of 2-amino-5-*o*-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole and different amines were carried out[15,16]. 2-Chloroacetyl-5-*o*-nitrophenyl derivative, yield 64%; m.p. 210°. Found: C, 40.0; H, 2.31; N, 18.70; S, 10.68. $C_{10}H_7N_4O_3SCl$ requires C, 40.10; H, 2.34; N, 18.72; S 10.70%. 2-Chloroacetyl 5-benzoylaminomethyl derivative, yield 66%; m.p. 202°. Found: C, 46.25; H, 3.50; N, 17.99; S, 10.25. $C_{12}H_{11}N_4O_2SCl$ requires C, 46.30; H, 3.53; N, 18.00; S 10.28%. All chloroacetylated aromatic amines gave correct N analysis.

Preparation of 2-α-arylaminoacetamido-5-o-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole[17] : 2-Chloroacetylamino-5-*o*-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole (0.1 *M*) was refluxed with different amines (0.12 *M*) in ethanol for 6 hr and product isolated. The physical constants are recorded in Table 1.

Preparation of α-carbamoylbenzylamino-5-o-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole : 2-Amino-5-*o*-nitrophenyl/benzoylaminomethyl-1,3,4-thiadiazole (0.1 *M*) was refluxed with different chloroacetylated amines (0.1 *M*) in ethanol for 8 hr and product isolated. The physical constants are recorded in Table 2.

TABLE 1—PREPARATION OF 2-4-ARYLAMINOACETAMIDO-5-o-NITROPHENYL/BENZOYLAMINOMETHYL-2,3,5-THIADIAZOLE

Sl. No.	R	R'	m.p. °C	Yield %	Diameter of zone of inhibition in mm S. aureus 24 hr	E. coli 24 hr
1.	Phenyl	o-Nitrophenyl	140	48	15	14
2.	o-Nitrophenyl	,,	80	50	10	—
3.	m-Nitrophenyl	,,	90	52	17	5
4.	p-Nitrophenyl	,,	188	54	12	—
5.	o-Tolyl	,,	80	55	12	—
6.	m-Tolyl	,,	75	47	13	—
7.	p-Tolyl	,,	108	59	8	—
8.	m-Hydroxyphenyl	,,	105	53	12	2
9.	p-Hydroxyphenyl	,,	117	52	17	2
10.	2,5-Dichlorophenyl	,,	340D	55	10	2
11.	Phenyl	Benzoylaminomethyl	120D	56	19	4
12.	o-Nitrophenyl	,,	68	59	16	5
13.	m-Nitrophenyl	,,	100	60	7	11
14.	p-Nitrophenyl	,,	160	57	8	2
15.	o-Tolyl	,,	100	61	11	2
16.	m-Tolyl	,,	130	64	5	—
17.	p-Tolyl	,,	200D	65	5	—
18.	o-Anisyl	,,	310	50	5	—
19.	p-Anisyl	,,	284	57	8	4
20.	p-Chlorophenyl	,,	274	59	16	—
21.	Cyclohexyl	,,	120	60	10	—

All compounds gave consistent nitrogen analysis.

TABLE 2—PREPARATION OF 2-4-CARBAMOYLBENZYLAMINO-5-o-NITROPHENYL/BENZOYLAMINOMETHYL-2,3,4-THIADIAZOLE

Sl. No.	R	R'	m.p. °C	Yield %	Diameter of zone of inhibition in mm S. aureus 24 hr	E. coli 24 hr
1.	Phenyl	o-Nitrophenyl	100	50	16	4
2.	o-Nitrophenyl	,,	190	52	12	6
3.	m-Nitrophenyl	,,	205	54	15	4
4.	p-Nitrophenyl	,,	200	55	14	6
5.	o-Chlorophenyl	,,	205	57	16	—
6.	p-Chlorophenyl	,,	133	53	10	—
7.	o-Anisyl	,,	105	54	10	—
8.	o-Tolyl	,,	190	60	10	—
9.	3,5-Dichlorophenyl	,,	175	59	14	9
10.	2-Naphthyl	,,	180	61	13	12
11.	Phenyl	Benzoylaminomethyl	140	63	8	10
12.	o-Nitrophenyl	,,	50	60	8	—
13	m-Nitrophenyl	,,	142	57	8	—
14.	p-Nitrophenyl	,,	175	65	7	2
15.	o-Tolyl	,,	275	68	9	—
16.	m-Tolyl	,,	86	69	10	—
17.	o-Anisyl	,,	180	63	12	—
18.	p-Anisyl	,,	160	61	15	—
19.	p-Chlorophenyl	,,	148	62	17	6
20.	2-Naphthyl	,,	195	64	10	9

All compounds gave consistent nitrogen analysis.

Preparation of arylcarbamoylmethylamino-5-o-nitrophenyl / benzoylaminomethyl-1,3,4-thiadiazole : The nitriles were prepared[18] which on further treatment with conc. H_2SO_4 at 0° gave corresponding amides.

The physical constants are recorded in (Table 3).

TABLE 3—PREPARATION OF 4-(5-o-NITROPHENYL/BENZOYLAMINOMETHYL-1,3,4-THIADIAZOL-2-YL-AMINO)-ARYLACETONITRILES

Sl. No	R	R'	m p °C	Yield %	Diameter of zone of inhibition in mm S. aureus 24 hr	E. coli 24 hr
1.	Phenyl	o-Nitrophenyl	205	50	7	—
2.	m-Nitrophenyl	,,	190	48	10	—
3.	Cinnamyl	,,	165	55	10	—
4	2-Hydroxyphenyl	,,	240	56	8	—
5.	3-Bromo-2-hydroxyphenyl	,,	285	59	8	—
6.	3,5-Dibromo-2-hydroxyphenyl	,,	165	60	15	—
7.	4-Hydroxy-3-methoxyphenyl	,,	225	61	12	—
8	5-Bromo-4-hydroxy-3-methoxyphenyl	,,	230	63	10	4
9	p-Anisyl	,,	200D	64	12	—
10.	Furfuryl	o-Nitrophenyl	320D	66	—	11
11.	Phenyl	Benzoylaminophenyl	100	50	10	—
12	m-Nitrophenyl	,,	110	55	9	—
13	Cinnamyl	,,	90	53	16	—
14.	2-Hydroxyphenyl	,,	180	54	8	—
15	3-Bromo-2-hydroxyphenyl	,,	200	59	18	—
16	3-5-Dibromo-2-hydroxyphenyl	,,	240	57	8	6
17.	4-Hydroxy-3-methoxyphenyl	,,	165	56	6	9
18.	5-Bromo-4-hydroxy-3-methoxyphenyl	,,	280	60	5	10
19.	p-Anisyl	,,	175	59	15	—
20.	Furfuryl	,,	199	56	8	—

All compounds gave consistent nitrogen analysis.

Antibacterial activity : The products were screened for antibacterial activity by cup-plate method[19], using DMF as solvent, at a concentration of 10 mg/ml. It was observed that all the compounds were moderately active against *S. aureus* but not against *E. coli* (recorded in the tables).

TABLE 4—PREPARATION OF 2-ARYLCARBAMOYLMETHYLAMINO-5-o-NITROPHENYL/BENZOYLAMINOMETHYL-1,3,4-THIADIAZOLE

Sl. No	R	R'	m.p. °C	Yield %	Diameter of zone of inhibition in mm S. aureus	E. coli
1.	Phenyl	o-Nitrophenyl	300D	47	10	—
2.	3-Nitrophenyl	,,	170	45	8	—
3.	Cinnamyl	,,	not melt	48	9	—
4.	2-Hydroxyphenyl	,,	not melt	50	11	—
5.	3-Bromo-2-hydroxyphenyl	,,	105	55	12	—
6.	3,5-Dibromo-2-hydroxyphenyl	,,	285	57	15	4

(Table 4 Contd.)

7. 4-Hydroxy-3-methoxyphenyl	,,	197	59	17	—
8 5-Bromo-4-hydroxy-3-methoxyphenyl	,,	215	60	10	4
9. *p*-Anisyl	,,	250	61	9	4
10. Furfuryl	,,	280	63	8	2
11. Phenyl	Benzoyl-amino-methyl	125	50	10	2
12. 3-Nitrophenyl	,,	150	51	12	2
13. Cinnamyl		195	53	14	5
14. 2-Hydroxyphenyl	,	205	55	14	-
15. 3-Bromo-2-hydroxyphenyl	,,	275D	57	10	
16 3,5-Dibromo-2-hydroxyphenyl	,	300	59	11	
17 4-Hydroxy-3-methoxyphenyl	,	235D	60	12	
18 5-Bromo-4-hydroxy-3-methoxyphenyl	,	265D	61	8	--
19. *p*-Anisyl	,	189	52	7	8
20 Furfuryl	,,	225D	53	10	9

All compounds gave consistent nitrogen analysis.

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Synthesis of New Dithiocarbamates as Potential Anthelmintic Antimicrobial and Insecticidal Agents

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Fourteen new N-aryl/alkyl/morpholino/piperidino/pyrrolidino dithiocarbamates have been synthesized as potent anthelmintic and were screened for anthelmintic activity against *Hymenolepis nana* infection in mice and insecticidal activity against male and female cockroaches (*Periplanata americana*) and two for antimicrobial activity. Few showed significant insecticidal activity.

THE growing incidence of helminthes infection in rural areas of various agriculture based countries has clearly demonstrated the urgent need of an ideal anthelmintic drug. Esters of dithiocarbamic acids have clearly been established as the leading anthelmintic[1,2,3], insecticidal and herbicidal[4] agents, and thiadiazoles are well known to possess nematocidal[5], insecticidal[6] and herbicidal[7] properties. Hence it was considered worthwhile to synthesize the title compounds anticipating that the resulting compounds may have considerable potency.

Experimental

Melting points were taken in open capillaries and are uncorrected.

Chloroacetyl-2-amino-5-methyl thiadiazole (I): These were prepared by the condensation of acetic acid with thiosemicarbazide according to known methods. Chloroacetylation in benzene yielded I[8,9].

Ammonium salts of dithiocarbamic acids (II). Aryl amines were treated with ammonia and carbon disulphide to yield II[10].

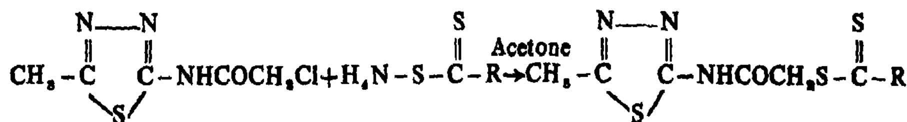
TABLE 1

Comp No.	R	m.p. °C	Yield %	Molecular formula
1	Phenyl amino	226	85	$C_{12}H_{12}N_4OS_3$
2	o-Tolyl amino	238	85	$C_{13}H_{14}N_4OS_3$
3	m-Tolyl amino	258	82	$C_{13}H_{14}N_4OS_3$
4	p-Tolyl amino	270	83	$C_{13}H_{14}N_4OS_3$
5	o-Anisyl amino	166	76	$C_{13}H_{14}N_4O_2S_3$
6	p-Anisyl amino	160	80	$C_{13}H_{14}N_4O_2S_3$
7	o-Chloro phenyl amino	209	81	$C_{12}H_{11}ClN_4OS_3$
8	m-Chloro phenyl amino	205	85	$C_{12}H_{11}ClN_4OS_3$
9	p-Chloro phenyl amino	215	81	$C_{12}H_{11}ClN_4OS_3$
10	Dimethyl amino	248	86	$C_8H_{12}N_4OS_3$
11	Diethyl amino	218	85	$C_{10}H_{16}N_4OS_3$
12	Morpholino	242	80	$C_{10}H_{14}N_4O_2S_3$
13	Piperidino	226	80	$C_{11}H_{16}N_4OS_3$
14	Pyrrolidino	252	82	$C_{10}H_{14}N_4OS_3$

Satisfactory C, H and N analyses (±0.4%) were obtained for all the compounds.

Results and Discussion

Insecticidal activity. The insecticidal activity was evaluated against adult male and female cockroaches (*P. americana*). The compounds were dissolved in acetone and the acetone solution



$$CH_3-C(=N-N=)C(-S-)-NHCOCH_2Cl + H_4N-S-\overset{S}{\overset{\|}{C}}-R \xrightarrow{\text{Acetone}} CH_3-C(=N-N=)C(-S-)-NHCOCH_2S-\overset{S}{\overset{\|}{C}}-R$$

S-(2-acetylamino-5-methyl 1,3,4-thiadiazolyl)-N-aryl/alkyl/morpholino/piperidino/pyrrolidino dithiocarbamates: Chloroacetyl-amino-5-methyl 1,3,4-thiadiazole (0.01 mole) was added with constant stirring to a solution of ammonium salt of N-aryl/alkyl/morpholino/piperidino pyrrolidino dithiocarbamic acids (0.01 mole) in 20 ml of aqueous acetone. The mixture was stirred at room temperature for 3 hr and evaporated to dryness. The residue was recrystallized from methanol to give the title compounds. The melting points and analytical data are recorded in Table 1.

applied at a dose of 0.02 ml of 0.5% and 0.1% solution per cockroach with 10 replications per compound. The chemicals were injected between 4th and 5th abdominal segment on the ventral side and the treated insects were kept under observation for 40 hr. The activity of the compounds were compared with well known insecticide ethyl parathion.

Out of the compounds tested, two compounds S-(2-acetylamino-5-methyl 1,3,4-thiadiazolyl)-N-pyrrolidino dithiocarbamate and S-(2-acetylamino-5-methyl 1,3,4-thiadiazolyl)-N-piperidino dithiocarbamates were found to be most active, with a mean

K. D. time of 6 and 10 hr, respectively. However, substitution by morpholine group decreased the insecticidal activity. Responses in case of the other amines were not significant.

Antifungal and antibacterial activity : Two compounds (Nos. 2 and 4) were tested for their antifungal and antibacterial activity but the response in both the cases was not significant.

Anthelmintic activity : All the compounds were tested against *H. nana* infection in mice according to the method of Witlock. These compounds were administered orally at a dose of 25 mg/kg with 10 replications per compound. After fasting for 24 hr the animals were dissected to count the worm present in the intestine but none of the compounds showed any significant activity.

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Potential Antineoplastic Agents : Synthetic and Pharmacological Studies on Some N-Aryl-N′-2(4-phenyl-5-arylazothiazolyl)thiocarbamides

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A number of compounds belonging to the series N-aryl-N′-2(4-phenyl-5-arylazothiazolyl) thiocarbamides have been synthesized by the condensation of corresponding 2-amino-4-phenyl-5-arylazothiazoles with different arylisothiocyanates respectively with a view to test their antitumor activity. The preliminary pharmacological investigations on the compounds have also been carried out.

DURING the last few years, there has been a growing interest in the synthesis and biological evaluation of compounds containing the N* – N* – S* or O* – N* – S* tridentate ligand system[1-5] or arylazogrouping[6,7]. This interest stems mainly from certain interesting biological activities[8,9], carcinostatic activities of heterocyclic carboxylaldehyde thiosemicarbazones and the interfering action of 5-arylazopyrimidines with nucleic acid synthesis. Moreover, various Schiff bases from benzaldehyde, nitrogenmustards and thiazoleamines have been reported to possess antitumor activity[10-12]. As a part of a general study directed towards the development of antineoplastic agents[13], the above rationale led to the examination of the synthesis and biological properties of N-aryl-N′-2-(4-phenyl-5-arylazothiazolyl) thiocarbamides having N* – N* – S* ligand system, arylazogrouping and a modified azomethine linkage[14-16].

The present communication deals with the synthesis of N-aryl-N′-2(4-phenyl-5-*o*-chlorophenylazothiazolyl)-, N-aryl-N′-2(4-phenyl-5-*m*-chlorophenylazothiazolyl)-, and N-aryl-N′-2(4-phenyl-5-*p*-chlorophenylazothiazolyl) thiocarbamides by the condensation of the corresponding 2-amino-4-phenyl-5-arylazothiazoles with appropriate arylisothiocyanates.

The precursor 2-amino-4-phenylthiazole was obtained by the condensation of acetophenone with thiourea in presence of iodine[17]. The arylazogroup at C-5 was introduced by the couplation of different diazonium salts.

On boiling equimolar quantities of arylisothiocyanates[18] and 2-amino-4-phenyl-5-arylazothiazoles in benzene on a steam bath, high yields of the corresponding N-aryl-N′-2[4-phenyl-5-(*o*, *m*, *p*-chlorophenyl)azothiazolyl]thiocarbamides (Table 1) were obtained. Purification was achieved by recrystallization with DMF-ethanol (1 : 1).

Experimental

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. IR spectra were obtained using KBr pellets and a Perkin-Elmer 720 Infracord spectrophotometer; bands reported were atleast of medium intensity. The results of elemental analyses were in good agreement with those of theoretical values.

2-Amino-4-phenylthiazole : It was prepared according to the method in the literature[17].

2-Amino-4-phenyl-5-o-chlorophenylazothiazole : Sodium nitrite (1.4 g; 0.02 mole) dissolved in water (25 ml) was gradually added to a well cooled solution of 2-chloroaniline (2.55 g; 0.02 mole) in 3 *N* HCl (2.5 ml). The diazonium salt solution was filtered in to a cold suspension of 2-amino-4-phenylthiazole (3.52 g; 0.02 mole) and sodium acetate (5 g) in ethanol (50 ml). After 2 hr, 2-amino-4-phenyl-5-*o*-chlorophenylazothiazole was filtered and washed several times with water. It was recrystallized as orange red needles from DMF-ethanol mixture (1 : 1), yield 4.70 g (75%), m.p. 215°.

2-Amino-4-phenyl-5-*m*-chlorophenylazothiazole and 2-amino-4-phenyl-5-*p*-chlorophenylazothiazole were also prepared by adopting a similar procedure.

N-phenyl-N′-2(4-phenyl-5-o-chlorophenylazothiazolyl) thiocarbamide : A mixture of phenylisothiocyanate (1.35 g; 0.01 mole) and 2-amino-4-phenyl-5-*o*-chlorophenylazothiazole (3.14 g; 0.01

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mole) in benzene (15 ml) was refluxed for 6-8 hr on a steam bath. The solvent was removed under reduced pressure and the residue was repeatedly washed with petroleum ether (40-60°). The crude thiocarbamide thus obtained was crystallized from DMF-ethanol mixture (1 : 1) as deep red needles, 3.77 g (84%), m.p. 199°. Anal. Found: C, 58.71; H, 3.53; N, 15.54; S, 14.21. Calcd. for $C_{22}H_{16}ClN_5S_2$; C, 58.73; H. 3.56; N, 15.57; S, 14.23%.

Similarly, other N-aryl-N'-2(4-phenyl-5-*o*-chlorophenylazothiazolyl) thiocarbamides were prepared by the condensation of 2-amino-4-phenyl-5-*o*-chlorophenylazothiazole with different arylisothiocyanates.

Using similar procedure as above several viz., N-aryl-N'-2(4-phenyl-5-*m*-chlorophenylazothiazolyl) thiocarbamides and N-aryl-N'-2(4-phenyl-5-*p*-chlorophenylazothiazolyl) thiocarbamides (Table 1) were obtained.

TABLE 1—SYNTHETIC AND PHARMACOLOGICAL SCREENING RESULTS OF N-ARYL-N'-2(4-PHENYL-5-ARYLAZOTHIAZOLYL) THIOCARBAMIDES AGAINST L-1210 LYMPHOID LEUKEMIA ASCITIC FLUID IMPLANTED INTRAPERITONEALLY IN BDF_1 MICE

Sl No	Compound* R'	R	Yield %	m.p. °C	Survivors+	T/C++ %
1.	2-Cl	H	84	199	6/6	101
2.	,,	2-CH_3	81	190	3/6	94
3.	,,	3-CH_3	72	210	5/6	95
4.	,,	4-CH_3	76	207	4/6	92
5	,,	2-OCH_3	82	216	5/6	103
6	,,	4-OCH_3	80	230	6/6	90
7	,,	2-Cl	78	227	4/6	95
8.	,,	3-Cl	75	285	3/6	98
9	,,	4-Cl	74	212	6/6	102
10.	,,	2-OC_2H_5	72	239	2/6	104
11	3-Cl	H	88	240	5/6	100
12	,,	2-CH_3	80	249	6/6	88
13.	,,	3-CH_3	82	230	5/6	96
14	,,	4-CH_3	85	256	4/6	102
15	,,	2-OCH_3	80	268	6/6	100
16	,,	4-OCH_3	84	262	4/6	105
17	,,	2-Cl	80	298	4/6	90
18	,,	3-Cl	78	245	5/6	95
19	,,	4-Cl	82	254	5/6	103
20	,,	2-OC_2H_5	85	283	6/6	107
21	4-Cl	H	85	250	4/6	99
22.	,,	2-CH_3	83	236	5/6	88
23	,,	3-CH_3	78	244	6/6	94
24.	,,	4-CH_3	80	260	6/6	100
25	,,	2-OCH_3	82	275	6/6	96
26.	,,	4-OCH_3	88	281	5/6	106
27	,,	2-Cl	85	292	4/6	98
28	,,	3-Cl	74	240	6/6	92
29.	,,	4-Cl	80	231	3/6	101
30.	,,	2-OC_2H_5	78	258	5/6	104

* Analytical results for C, H, N and S for these compounds agreed within ±0.5% of the theoretical values.

\+ All doses for these compounds were 400 mg/kg

++ Ratio of mean survival time of test animals (T) to control (C). Mean survival time of control is 30 days

These N-aryl-N'-2(4-phenyl-5-arylazothiazolyl) thiocarbamides were characterized on the basis of their elemental analyses and the presence of characteristic bands N=N (1615 cm^{-1}), NH (3400 cm^{-1}), N=C=S (1520 cm^{-1}) and substituted benzene ring (760 cm^{-1}) in their ir spectra.

Biological results:

In L-1210 leukemia, BDF_1 mice were inoculated intraperitoneally with 10^6 tumor cells. The index of evaluation for the ascitic tumor is T/C [(mean survival time of treated mice/mean survival time of control mice)×100]. For L-1210, a T/C $\geq$ 125 is considered positive. The finely ground drugs were suspended in a solution of sterile distilled water with a drop of Tween-80. The drugs were given daily intraperitoneally at approximately the maximum tolerated doses, starting 24 hr after tumor inoculation. The detailed methods for the evaluation of antitumor activity in mice have been described elsewhere[19-21].

Shown in Table 1 are the data of antitumor activity against L-1210 leukemia. It appears from this primary screening that the level of toxicity varied greatly in this group. Although all the compounds were found to be practically inactive, some compounds viz. Nos. 5, 10, 16, 20, 26 and 30 were somewhat more potent than the other members of this series.

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Effects of Ultraviolet Radiation on Amino Acid Composition of Single Cell Protein

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Effects of ultraviolet radiation upon the viability and amino acid composition of *Saccharomyces cerevisiae* and *Candida utilis*, used for single-cell protein (SCP) production, have been studied. A slight difference in the radiation resistance of the two species was found. Radiation doses up to 75 sec seemed to have marginal degrading effect on the various amino acids present in the SCP products. The contents of protein was also not significantly changed.

A review of literature shows that only a few attempts have been made to study the effects of radiation on the preservation of single-cell protein (SCP)[1-5]. One important requirement for microorganisms selected for SCP production from various substrates is that of non-pathogenicity. The heating to which the product is subjected during processing should be strong enough to kill a substantial fraction of the viable cells. Intense heat may, however, affect various nutritional components of the SCP products. It is, therefore, necessary that sterilization processes should be considered carefully, either without or in combination with heat treatment.

The present investigation was undertaken with a view to study the effects of ultraviolet radiation upon the viability of cells and amino acid composition of the SCP products of two microbial strains, namely *Saccharomyces cerevisiae* and *Candida utilis*, used for SCP production.

Experimental

Materials and Methods ·

Microorganisms and medium : The organisms *Saccharomyces cerevisiae* and *Candida utilis* were procured from the Department of Botany, University of Allahabad, Allahabad. These cultures were maintained by monthly transfer on glucose-yeast extract agar medium and were stored at low temperature for further use.

For irradiation, the organisms were grown in 2% glucose-yeast extract-peptone water (YP water) for 72 hr at 30°. 10 ml of the cell containing material (approximately 10^7 cells/ml) were pipetted into a sterilized petridish and irradiated with the lid of the dish removed. The viability of the cells, of the non-irradiated controls kept at ambient temperature, and of the irradiated samples, was examined by the surface count method using Sabouraud's agar and incubation for 48 hr at 30°.

Irradiation : For irradiating the microorganisms, a UV lamp (Cat. No. CM 03106 ser. N 0232, Toshniwal, India) was used. The wavelength range of the source was 3900-4300 Å. The samples (1.0 g/l biomass) were placed at fixed distance (30 cm) from the source and doses were varied in respect of time. Thus, the cell suspensions were irradiated for 15, 30, 45, 60 and 75 sec.

The crude protein was estimated by the method of MacKenzie and Wallace[6]. The amino acid analysis of the protein was done with a Beckman Model 116 amino acid analyser (operated according to principles described by Spackman *et al*[7]) after hydrolysis according to the method of Weidner and Eggvin[8].

Results and Discussion

The inactivation of cells of *S. cerevisiae* and *C. utilis*, when irradiated with ultraviolet rays is shown in Figs. 1 and 2. It is seen from the figures that a successive decrease occurred in the survival pattern of the cells with increase in the dose of irradiation.

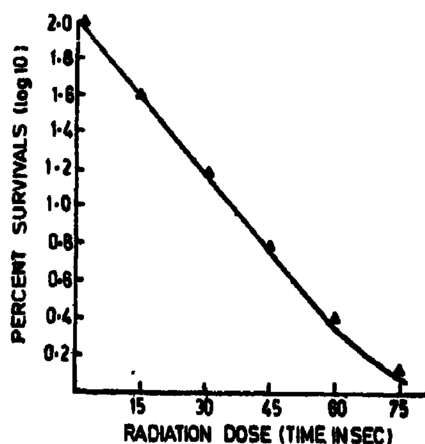


Fig. 1

Protein content : The total protein content of irradiated and non-irradiated samples are recorded in Table 1. Tables 2 and 3 show the effect of

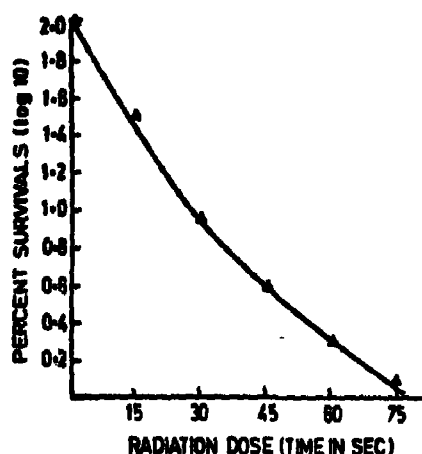


Fig. 2

TABLE 1—COMPARISON OF PROTEIN CONTENTS OF NON-IRRADIATED AND IRRADIATED CELLS OF *Saccharomyces cerevisiae* AND *Candida utilis*

Organism	Total protein content of dry cell mass (%)					
	Non-irradiated	Irradiated (time in sec)				
		15	30	45	60	75
S. cerevisiae	45.5	45 2	45 1	44.8	45.0	44 7
C. utilis	45.0	45.0	44.8	44.6	44.7	44 6

TABLE 2—AMINO ACID COMPOSITION OF NON-IRRADIATED AND IRRADIATED SCP PRODUCTS OF *Saccharomyces cerevisiae* (g/16 g N)

	Amino acids	Non-irradiated	Irradiation dose (sec)				
			15	30	45	60	75
Essential amino acids	Lysine	8 30	7 70	7.61	7 20	7 00	6 85
	Threonine	7.65	7 90	7 83	7 69	7.50	7 01
	Valine	6 97	7 86	7 62	7 18	6.95	7 13
	Methionine	—	—	—	—	—	—
	Isoleucine	6 41	7.00	7 29	7.41	7.41	7 49
	Phenylalanine	5 15	5.71	6 43	5.32	5.48	4.89
	Tryptophan	—	—	—	—	—	—
Non-essential amino acids	Alanine	8 87	8.99	8.78	9.00	7 77	8 30
	Arginine	4.98	5 25	4 91	4 39	5.10	5 00
	Aspartic acid	14.93	15 00	14 57	14 50	14 30	14.42
	Cysteine	1.72	1 74	1.70	1 78	1 78	1 80
	Glutamic acid	14 69	14.92	14 71	15 30	14 71	15 00
	Glycine	5 88	6 63	5 87	6 37	5 78	6.06
	Histidine	1 58	2 40	1.90	1 73	1 89	1 98
	Proline	—	—	—	—	—	—
	Serine	6 67	7 00	6 37	6.25	5 82	5 84
	Tyrosine	1.74	2 00	1 75	1 80	1 97	1 72

irradiation on amino acids in SCP products of *S. cerevisiae* and *C. utilis*. Methionine, proline and tryptophan could not be detected with the analytical method used. No nutritional evaluations was done.

TABLE 3—AMINO ACID COMPOSITION OF NON-IRRADIATED AND IRRADIATED SCP PRODUCTS OF *Candida utilis* (g/16 g N)

	Amino acids	Non-irradiated	Irradiation dose (sec)				
			15	30	45	60	75
Essential amino acids	Lysine	6 86	7 85	6 66	7 52	6.42	7.19
	Threonine	5 86	5 40	5 90	5 94	5 61	6.48
	Valine	5 66	6.18	7 75	4 43	5 81	5.61
	Methionine	—	—	—	—	—	—
	Isoleucine	5 50	5 37	5.80	4 41	4 57	5.65
	Phenylalanine	4 20	3 36	4 08	3 70	3.59	3.10
	Tryptophan	—	—	—	—	—	—
Non-essential amino acids	Alanine	7 71	8.00	7 42	8.03	7 78	8 08
	Arginine	5 00	4 93	4 77	4 00	4 31	4.53
	Aspartic acid	13 00	12 00	11.00	10 58	11 82	11.42
	Crysteine	1 35	1 30	1.36	1 36	1 30	1 31
	Glutamic acid	20 12	19 68	19 61	24.01	22 18	22 11
	Glycine	4 83	4.61	5 21	5 23	5 29	5 26
	Histidine	2 38	2 98	2.89	2 67	2 63	2 32
	Proline	—	—	—	—	—	—
	Serine	7 18	7 02	5.98	6 77	5 78	6 08
	Tyrosine	3 08	3 12	3 45	3 44	3 46	2 99

It is seen that in both the cases destruction of amino acids increased with increase in irradiation time, and total protein content of irradiated samples was less than that of non-irradiated products. Lysine content of *S cerevisiae* decreased slightly on 15 sec irradiation dose, but it increased in case of *C. utilis*.

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Spectrophotometric Determination of Rhenium with N-(4-Methoxy-phenyl)-α-thiopicolinamide and Evaluation of the Stability Constant of the Complex Involved Therein

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Rhenium reacts with N-(4-methoxy-phenyl)-α-thiopicolinamide to form a stable reddish brown complex on reduction with stannous chloride in 1.08 M to 1.32 M hydrochloric acid medium and the metal can be estimated by extractive photometry in chloroform medium. The system obeys Beer's law from 1-12 ppm at 430 nm. The molar absorptivity is 7.43×10^3 and the Sandell's sensitivity is 0.025 μg cm^{-2}. The metal forms a 1 : 2 complex (metal to ligand) with the ligand. Stability constant (log K) of the Re-complex has been evaluated by the Leden (7.60) and Rossotti and Rossotti (7.99) methods.

OF the existing spectrophotometric methods of determination of rhenium, those utilizing thiocyanate, some sulphur bearing organic reagents[1-4], and some oximes are of particular importance in analytical chemistry

The present work describes the use of extractive photometric determination of rhenium with N-(4-methoxy-phenyl)-α-thiopicolinamide. Rhenium forms a reddish brown complex in 1.08-1.32 M HCl medium in presence of $SnCl_2$. The metal forms 1 : 2 complex as determined by Job's and molar ratio methods. The equilibrium constant has been evaluated by extending Leden's and Rossotti-Rossotti's method by graphical extrapolation using spectrophotometric data.

Experimental

A Hilger Uvispek spectrophotometer with 10 mm quartz transmission cells was used.

The standard rhenium(VII) solution was prepared by dissolving an accurately weighed quantity of potassium perrhenate (Johnson Matthey) in double distilled water. The solution was standardised by nitron method.

A 0.05% (w/v) solution of N-(4-methoxy-phenyl)-α-thiopicolinamide was prepared in absolute ethanol.

0.6694 M solution of stannous chloride (G. R., E. Merck) was prepared in 1 M hydrochloric acid.

Standard solutions of diverse ions were prepared from their chloride or sulphate, or from sodium, potassium or ammonium salts. All other chemicals were of AR grade. Double distilled water was used for preparing the solutions.

Recommended procedure : 5 ml of 0.05% (w/v) reagent solution in absolute ethanol was added to a standard solution of perrhenate (0.75 ml of 0.25 mg/ml rhenium) in a beaker followed by 2.5 ml of 0.6694 M stannous chloride solution and hydrochloric acid to maintain the final acidity between 1.08-1.32 M. At subsequent measurements, final acidity was maintained at 1.2 M with HCl. The solution was diluted to 25 ml with the addition of measured quantity of water and ethanol in the ratio of 1 : 1. The mixture was warmed for 5 min at 60-70°, cooled and transferred to a separatory funnel The mixture was then shaken with 12 ml of chloroform for 5 min The settled chloroform layer was collected. The aqueous phase was washed twice, each time with 5 ml of chloroform. The combined extract and washings were dried over anhydrous sodium sulphate and transferred to 25 ml volumetric flask and diluted up to the mark with chloroform. This order was maintained throughout this work. A reagent blank without the addition of rhenium was also run. Absorbance of the complex against reagent blank and also that of the reagent against chloroform blank was measured at various wavelengths. The complex showed maximum absorbance at 430 nm.

Results and Discussion

The full colour development of the complex was obtained after heating for 5 min at 60°-70°.

The colour intensity remained constant for 5 hr and the period of complete extraction in chloroform was 5 min.

4 ml of 0.05% reagent solution in absolute ethanol was quite enough for the full colour development of 10 ppm of rhenium.

Addition of more reagent did not produce any adverse effect on the colour system. For subsequent measurements 5 ml of the reagent solution was used. For maximum colour development, 1.08-1.32 M HCl medium was required.

It has been observed that 1.5 ml of 0.6694 *M* stannous chloride solution was sufficient for full colour development though a higher concentration of the latter had no adverse effect. A 0.6694 *M* $SnCl_2$ solution was however always used.

Validity of Beer's law, relative error, sensitivity and molar absorptivity : Test solutions with different concentrations of rhenium were prepared by the recommended procedure. The system adheres to Beer's law from 1-12 ppm.

The Ringbom's[4] optimal concentration range for measurement was found to be from 3.72 11.5 ppm.

The relative error per 2% absolute photometric error[6] was found to be 2.72.

The molar absorptivity as obtained from Beer's law is 7.43×10^3 at 430 nm and Sandell's sensitivity[7] is 0.025 $\mu g\ cm^{-2}$.

Composition of the complex The composition of the complex was determined by Job's method of continuous variation[8] and by the mole-ratio method[9]. For Job's method, mixture (12 ml total) of equimolar solutions (5.37×10^{-4} *M*) of the perrhenate and the reagent were treated as in the general procedure. The curve indicated that the complex contained rhenium and the reagent in the ratio 1 : 2. This result was confirmed by the mole-ratio method.

Effect of diverse ions : The effect of diverse ions on the determination of rhenium was studied by adding a definite amount of foreign ion to a solution containing 10 ppm of rhenium and working as under the recommended procedure. The results are shown in Table 1.

TABLE 1—EFFECT OF DIVERSE IONS, Re=10 ppm

Ions	Amount studied ppm	Ions	Amount studied ppm
U(VI)	400	Cd(II)	400
Th(IV)	400	Ca(II)	400
Mo(VI)	60	Ir(III)	Interferes
W(VI)	200	Oxalate	400
V(V)	Interferes	EDTA	400
Pt(IV)	Interferes	Tartrate	400
Pd(II)	Interferes	Citrate	400
Mn(II)	400	F^-	Interferes
Cu(II) EDTA	400	SCN^-	Interferes
Co(II) EDTA	400	BO_3^-	Interferes
Fe(II) Oxalate	200	SO_4^{2-}	400
Ni(II)	400	NO_3^-	400
Zn(II)	400	PO_4^{3-}	400

Stepwise formation constants : The procedure for evaluation of the stepwise formation constants was examined by proper extension of Leden's method and verified by the method of Rossotti-Rossotti.

Leden's method[10] *:* For evaluation of K_1 and K_2 we have assumed that the equilibrium concentrations of the ligand is equal to total ligand concentration. This assumption is found to be valid as is evident from the values of free ligand concentration calculated for each determination of absorbance.

The successive stability values obtained by considering the degree of complexation are given below :

$$\lim_{L\to0}\psi_1=\lim_{L\to0}\frac{\phi-1}{L}=\beta_1=4.0\times10^3$$

The plot of ψ_1 against free ligand concentration gave a straight line of intercept $\beta_1=4.0\times10^3$ (Fig. 1).

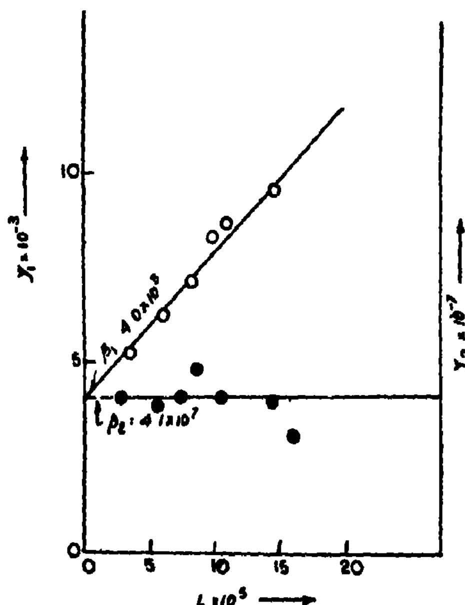


Fig 1 Leden's method of stability constant Re – N(4-methoxyphenyl) α-thiopicolinamide

Similarly, by substituting the value of β_1 in the following function

$$\lim_{L\to0}\psi_2=\lim_{L\to0}\frac{\psi_1-\beta_1}{L}=\beta_2=4.1\times10^7$$

The plot of ψ_2 against free ligand concentration gave a straight line of intercept β_2 (Fig. 1), the overall stability constant. The values of K_1 and K_2 are found to be

$K_1=4.0\times10^3$; $K_2=1.0\times10^4$

The results are tabulated in Table 2.

TABLE 2—OVERALL STABILITY CONSTANT AND STEPWISE FORMATION CONSTANT OF THE COMPLEX AT 27°

Methods	Log K_1	Log K_2	Log $K_{overall}$
Leden	3.60	4.00	7.60
Rossotti-Rossotti	3 95	4.04	7 99

Rossotti-Rossotti's method[11] *:* This method is based on the absorbance of a complex dependent on the total concentrations of ligand and central

group. When only the two complexes are formed, β_1 and β_2 may be calculated from the following equations :

$$\xi = \frac{A_S - \gamma \epsilon_L[L]}{C_M[L]} = \frac{\epsilon_0 + \epsilon_1\beta_1[L]}{1+\beta_1[L]} \quad .. \quad (i)$$

$$\xi = \frac{A_S - \gamma \epsilon_L[L]}{C_M[L]} = \frac{\epsilon_0 + \epsilon_1\beta_1[L] + \epsilon_2\beta_2[L]^2}{1+\beta_1[L]+\beta_2[L]^2} \quad (ii)$$

The plot of ξ against $\frac{\xi - \epsilon_0}{L}$ gave a straight line of slope $-\beta_1$ and intercept ϵ_1 for the complex.

The values of β_1 and ϵ_1 are found to be (Fig. 2)

$\beta_1 = 9 \times 10^3$; $\epsilon_1 = 7.5 \times 10^3$.

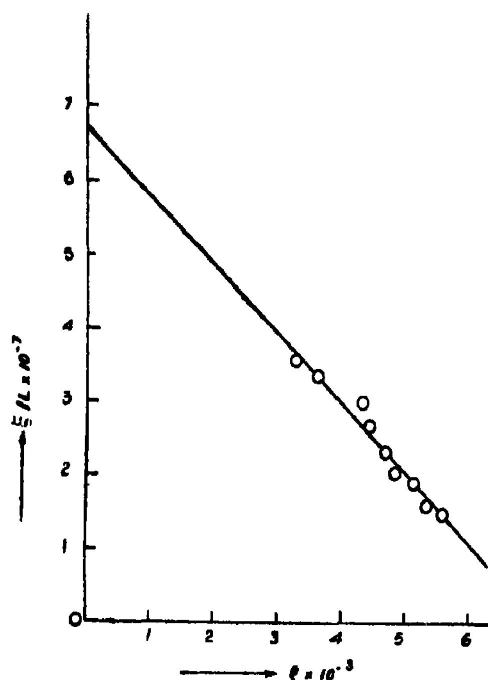


Fig 2. Rossotti-Rossotti's method of stability constant Re-N(4-methoxy-phenyl) ∝-thiopicolinamide

These values of β_1 and ϵ_1 were further substituted in equation (ii) which was solved as below :

$$\frac{\epsilon_0 - \xi}{\xi L} + \frac{\epsilon_1 - \xi}{\xi L}\beta_1 = \beta_2 - \frac{\epsilon_2\beta_2}{\xi} \quad (iii)$$

The plot of $\frac{\epsilon_1 - \xi}{\xi L}\beta_1 - \frac{1}{L^2}$ against $1/\xi$ gave straight line of slope $-\epsilon_2\,\beta_2$ and intercept β_2 for the complex.

The values of β_2 and ϵ_2 are found to be (Fig. 3)

$\beta_2 = 90.0 \times 10^6$; $\epsilon_2 = 4.14 \times 10^4$.

The values of K_1 and K_2 are given below

$K_1 = 9 \times 10^3$; $K_2 = 1.17 \times 10^4$

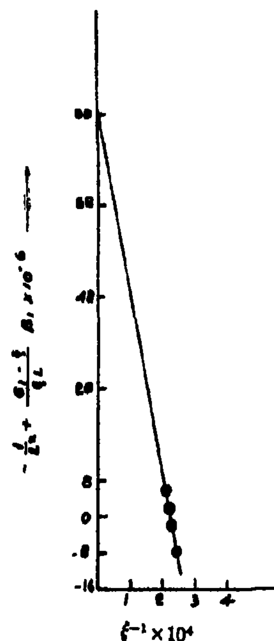


Fig 3 Rossotti-Rossotti method of stability constant. Re-N(4-methoxy-phenyl) ∝-thiopicolinamide complex

The values of overall stability constant obtained by Leden's method and Rossotti-Rossotti method are summarized in Table 2.

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Phenoxy Acetyl Acetophenone as an Analytical Reagent for Iron

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A new spectrophotometric method for the microdetermination of iron using phenoxy acetyl acetophenone is described. The complex is formed instantaneously, in cold and at pH 5.5. It can be extracted in toluene and shows maximum absorbance at 390 nm. Beer's law is valid over the range of 0.5 – 8.0 µg Fe/ml. The complex is stable and sensitivity of determination is 0.0081 µg Fe/cm². Many common ions are tolerated to a large extent. The method is simple and can be used satisfactorily for the determination of iron in drugs and ores.

SEVERAL reagents have been proposed for the spectrophotometric determination of iron[1,2]. The metal is known to be present in small amounts in various synthetic and natural objects and investigations are now mainly centred in suggesting new methods for estimation of iron in trace quantity in such objects. Some very sensitive reagents are recently reported for its estimation in ores, alloys, water, drugs and biological materials[3-9].

In the present studies, a new diketone compound, phenoxy acetyl acetophenone (PAA), has been investigated as an analytical reagent for trace determination of iron in drugs and ores. The reagent was synthesized and used. It forms a yellowish red complex with Fe(II) as well as Fe(III). The complex is extractable in toluene and shows maximum absorbance at 390 nm. The colour development is instantaneous and there is negligible interference from other transition metals commonly associated with iron. The reagent is sensitive and can be used to determine iron in drugs and ores.

Experimental

Beckman DU-2 spectrophotometer with quartz cuvettes of 1 cm thickness was used for spectrophotometric measurements.

Iron(II) solution (0.05 *M*) was prepared by dissolving a known weight of ferrous ammonium sulphate (A. R.) in distilled water and was standardized[10]. Solutions used in the studies contained 25 µg Fe/ml. Fresh solutions were always used.

Acetate buffer, *p*H 5.5 was prepared by taking appropriate quantities of 1 *M* solutions of sodium acetate and acetic acid.

The reagent PAA was synthesized from phenoxy acetic acid. This acid itself was prepared by the reaction of phenol and chloroacetic acid in NaOH[11]. The ethyl ester of phenoxy acetic acid, when treated with acetophenone in presence of potassium *tert*-butoxide underwent Stobbe condensation to yield pinkish white phenoxy acetyl acetophenone[12]. It was crystallized from ethyl alcohol. (Found: C, 75.45; H, 5.58. Calcd. C, 75.59; H, 5.51%; m.p. 80°). 5 ml of 1.77×10^{-3} *M* solution of PAA in acetone was used in the studies.

Ore samples were obtained from Indian Bureau of Mines, Nagpur.

General procedure. An aliquot of solution containing 5 to 80 µg of iron was taken in a beaker. 10 ml of acetate buffer of *p*H 5.5 was added and the total volume was made upto 20 ml with distilled water. To it was added 5 ml of 1.77×10^{-3} *M* solution of PAA in acetone. The yellowish orange Fe-PAA complex formed instantaneously. The solution was transferred to a separatory funnel and equilibrated for 30 sec with 10 ml toluene. The organic layer was separated and its absorbance was read at 390 nm against a reagent blank prepared in an identical manner. The concentration of iron in an unknown solution was calculated with the help of a calibration curve.

Results and Discussion

Optimum conditions. The complexation reaction is instantaneous and takes place in cold. One extraction with 10 ml of toluene and shaking period of 30 sec is sufficient for quantitative extraction of iron. The complex is highly stable; the absorbance remains constant for 8 days. The extraction behaviour of Fe-PAA complex as a function of *p*H was studied. It is found that extraction is quantitative between *p*H 5.0-6.0. Sodium acetate-acetic acid buffer is most suitable to maintain the *p*H and 10 ml of acetate buffer of *p*H 5.5 was used in the studies. The result remains unaffected even if the volume of buffer is varied from 5 to 15 ml. Potassium hydrogen phthalate – NaOH and sodium hydrogen phosphate-potassium dihydrogen phosphate buffers are also suitable for quantitative extraction while with sodium citrate – NaOH buffer of *p*H 5.5 extraction is found to be 36% only. 5 ml of 1.77×10^{-3} *M* PAA solution in acetone (metal

reagent ratio 1 : 20) is necessary for complete complexation. Excess of reagent does not make any difference in the absorbance. Toluene and ethyl acetate quantitatively extract the iron-complex while other solvents such as chloroform, carbon tetrachloride, benzene, *n*-hexanol, *n*-butanol and *n*-amyl alcohol give a lower absorbance.

Spectral characteristics : The spectra of Fe-PAA complex against reagent blank is shown in Fig. 1. It shows two maxima ; one at 390 nm and another at 450 nm. The λ_{max} at 390 nm is more prominent and hence all the measurements were made at 390 nm. Under the conditions, the reagent alone does not show any absorbance against the solvent blank. Both Fe(II) and Fe(III) react identically with the reagent The range in which Beer's law is followed is found to be from 0 5-8.0 μg Fe/ml. The optimum range of iron determination as evaluated from Ringbom plot is 1.0-7.9 μg Fe/ml. Sandell's sensitivity and molar absorptivity are 0.0081 μg Fe/cm^2 and 6.813×10^3 l.mole^{-1} cm^{-1}, respectively From 10 different sets of observations, the relative standard deviation was found to be 1.6%.

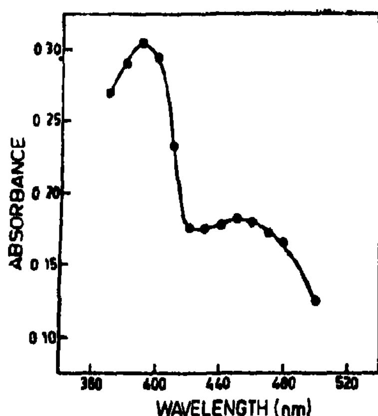


Fig 1 Absorption spectra.
Fe = 25 μg, pH - 5 5, 5 ml of 1.77×10^{-3} *M* PAA

Effect of diverse ions : Several foreign ions were examined for their effect on the extraction behaviour of iron. The tolerance limit was calculated as that amount of foreign ion required to cause a $\pm 2\%$ error in the recovery of iron. The results are given in Table 1. EDTA interferes strongly in the determination and must not be present. Many transition metals generally associated with iron in alloys, ores etc. were found to be tolerated upto very high concentration.

Determination of iron in drugs : Iron present in drugs in the form of ferrous sulphate, ferrous succinate and ferrous fumarate can be conveniently determined by this method. For this, tablets or capsules containing iron in the form of ferrous sulphate or ferrous succinate were placed in a beaker. To it was added 50 ml of distilled water containing 2 to 3 ml of conc. HCl and the mixture was boiled until complete dissolution occurred. The boiling mixture was filtered through a filter paper previously rinsed with distilled water. The residue was washed with 20 ml of boiling distilled water and the final volume of filtrate was made upto 250 ml in a volumetric flask with distilled water. In case of tablet or capsule containing iron as ferrous fumarate, digestion with 20 ml of conc H_2SO_4 for 2-3 hr in a Kjeldahl flask was carried out. The solution was transferred to a beaker, concentrated to about 1 ml, cooled and diluted with distilled water. Insoluble matter was removed by filtration and the filtrate was made upto 250 ml in a volumatric flask with distilled water. In case of liquid samples, 2 ml of the liquid was diluted with distilled water in a 250 ml volumetric flask containing 2 ml of conc. HCl. In all cases, solution containing nearly 25 μg of iron per ml was prepared by suitable dilution and the procedure was followed. 10 tablets/capsules or liquid portions were taken in each case and experiments were performed 4 times. In every case, the result obtained was compared with the standard O-phenanthroline method for iron estimation[1,2]. The results obtained are given in Table 2.

TABLE 1—EFFECT OF DIVERSE IONS

Fe = 25 μg, pH = 5 5, λ = 390 nm

Ion present	Tolerance limit (μg)	Ion present	Tolerance limit (μg)
Cl^-	17700	Ag^+	4300
I^-	5050	Mg^{2+}	1900
SCN^-	2300	Mn^{2+}	2200
SO_4^{2-}	5800	Co^{2+}	3550
$S_2O_3^{2-}$	6700	Ni^{2+}	2000
$Cr_2O_7^{2-}$	21600	Cu^{2+}	2550
oxalate	3500	Zn^{2+}	2600
citrate	5600	Hg^{2+}	6000
tartrate	5900	Pb^{2+}	8300
EDTA	None	Al^{3+}	54

TABLE 2—DETERMINATION OF IRON IN DRUGS

Name of the drug	Manufacturor	Iron present as	Iron* present (mg)	Iron found (mg)	%Error
Iberol	Abbott Laboratories	Ferrous sulphate	105 00	106 00	0.95
Tablets of FeSO$_4$ and Folic Acid	Enpharma Laboratories	Ferrous sulphate	12 08	11 95	1.07
Folinate	Alembic Chemicals	Ferrous fumarate	82.13	82.13	0 00
Geriatone	Alembic Chemicals	Ferrous sulphate	12 08	12 26	1.49
Hematrine	Sandoz Pharmaceuticals	Ferrous succinate	32.94	31.93	3.00
Becadexamine	Glaxo Laboratories	Ferrous fumarate	16.42	16.25	1.03
Compoferon	Bayer India Ltd	Ferrous sulphate	60 28	59.45	1.37
Fesofar	Reptakos Brett and Co	Ferrous sulphate	30.21	30 12	0.29
Siderfol	Smith, Kline and French Co.	Ferrous fumarate	98 82	97.9	0 93
Iberol	Abbott Laboratories	Ferrous sulphate	26.25	26.25	0.00

* O-phenanthroline method.

Determination of iron in ores :

Procedure : About 0.4 g of sample (120 mesh) was weighed accurately and dissolved in a mixture of conc. HCl and HNO_3 (15+10 ml). The solution was heated till all the nitrous fumes were removed. 20 ml of 1 : 1 H_2SO_4 was added and the solution was evaporated almost to dryness. 50 ml of distilled water was added and the residue was digested till all the salts dissolved. It was cooled and filtered through a filter paper previously rinsed with distilled water. The working solution (nearly 25 μg Fe/ml) was prepared by appropriate dilution of this solution. 1 ml of this solution was taken and the procedure was followed. The experiments were performed with 10 different portions of solutions and the results were compared with standard O-phenanthroline method[1,8]. The results obtained are given in Table 3.

TABLE 3—DETERMINATION OF IRON IN ORES

Ore	Iron present* %	Iron found %	% Error
Sample 1	50.26	50 59	0 33
Sample 2	39 41	39 50	0 09

* O-phenanthroline method

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Selective Extraction and Spectrophotometric Determination of Iron(III) as Thiocyanato and Azido Mixed-Complexes with Hydroxy-amidine

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A simple, rapid and selective method for solvent extraction and subsequent spectrophotometric determination of microamounts of iron(III) as thiocyanato and azido mixed-complexes with a newly synthesized extractant, N-hydroxy-N-*m*-chlorophenyl-N'-(2,3-dimethyl)phenylbenzamidine hydrochloride (HOAm) is described. The ratio of chelating extractant and azide or thiocyanate to metal in mixed complex is found to be 1 : 1 · 2 (Fe : HOAm : N_3^-/SCN^-) in benzene. The molar absorbances of azido and thiocyanato mixed-complexes are 4,000 and 12,000 $l.mole^{-1}cm^{-1}$ at 520 and 460 nm respectively. The thiocyanato mixed complex can be extracted quantitatively from 0.1 to 0.4 *M* HCl. The tolerance of the method to other ions is given.

A number of reagents[1-6] have been described for the colorimetric determination of iron. The most widely used reagent for iron(III) is thiocyanate. Although the method is simple, it suffers from various limitations such as variation of colour intensity with respect to the concentration of thiocyanate and hydrochloric acid. Several modifications have been suggested to improve the method. Recently, mixed-ligand complex of iron(III) with N-hydroxyethylenediamine-N,N',N'-triacetate and thiocyanate has been reported by Yamamoto and Ohashi[6]. The method is fairly selective, but is less sensitive than the parent thiocyanate method.

N-hydroxy-N,N'-diarylbenzamidines have been found to be potential analytical reagents for the determination of various transition elements[7-12]. In this communication, we report a simple, rapid and selective method for the extractive spectrophotometric determination of micro amounts of iron(III) with the newly synthesized reagent, N-hydroxy-N-*m*-chlorophenyl-N'-(2,3-dimethyl)phenylbenzamidine hydrochloride (HOAm), in the presence of thiocyanate and azide. This method has a wider working range of reagent concentration and Beer's law and shorter standing time. The method has been applied for the determination of iron in drugs.

Experimental

Apparatus : An ECIL UV-VIS spectrophotometer model GS-865, with matched 1 cm silica cells, were used for absorbance measurements. A systronic *p*H meter type-322 was used for *p*H measurements.

Reagent and chemicals All the chemicals used were of B. D. H., AnalaR grade. The stock solution of iron was prepared by dissolving iron wire (E. Merck) in 30% nitric acid. The oxides of nitrogen were removed by boiling and the solution was standardised gravimetrically[13]. A 0.1% w/v solution of the reagent[7,14] was used for extraction purposes.

Procedure : A measured amount of iron(III) was introduced into a 100 ml separatory funnel and was mixed with 2 ml potassium thiocyanate or sodium azide solution (2% w/v), the acidity was adjusted to the required value and the solution diluted with water to 25 ml. The aqueous phase was equilibrated with 25 ml benzene solution of the reagent for 2 min and the organic layer was dried over anhydrous sodium sulphate (2 g) for a few min in a 50 ml beaker. The absorbance was measured at respective λ_{max} against reagent blank.

Results and Discussion

Absorption spectra : The reagent showed negligible absorption in the region 450-700 nm. The red-orange thiocyanato and red-purple azido mixed-complexes showed λ_{max} at 460 and 520 nm, respectively. Their relevant spectral data are shown in Table 1.

Effect of variables : Of the various solvents (benzene, chloroform, carbontetrachloride, esters, ethers and alcohols) used, benzene was preferred because the distribution coefficient of metal as complex was high. The acidity of the aqueous phase was maintained with 2 *M* hydrochloric acid and dilute ammonia. Acetic, nitric and sulphuric acids could not be used due to low absorbance of

* For correspondence.

TABLE 1—SPECTRAL DATA FOR THIOCYANATO AND AZIDO MIXED-COMPLEXES OF IRON(III) WITH HOAm IN BENZENE

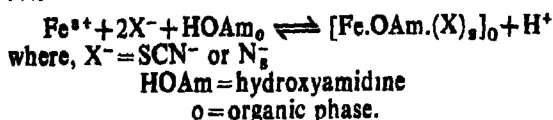
Characteristics	Thiocyanate system	Azide system
Optimum acidity (*M* HCl)/*p*H	0.1-0.4 *M* HCl	4.0-4.8
Colour	Red-orange	Red-purple
λ_{max}, nm	460	520
ϵ, l. $mole^{-1} cm^{-1}$	12,000	4,000
Sandell's sensitivity µg of Fe^{3+} per cm^2	0.0046	0.0139
Optimum concentration range on the basis of Beer's law, ppm	0.2-4.0	0.8-13.0
Relative standard deviation*	±0.7%	±0.8%

* 10 measurements, each containing 2 ppm Fe^{3+} in thiocyanate or 6 ppm Fe^{3+} in azide system.

the complex. The optimum acidity ranges are shown in Table 1.

A 50 and 200 fold molar excess of hydroxyamidine and thiocyanate or azide respectively were adequate for complete extraction of iron(III). Addition of more reagents caused no adverse effect on the absorbance of the coloured system. The order in which the reagents are mixed was not critical. An equilibrium period of 2 min was sufficient for complete extraction of metal as complex. The extracts were stable for at least 30 hr at 27°. The variation in temperature from 20 to 40° and volume of the aqueous phase from 15 to 60 ml did not affect the optical properties of the mixed-complex. No effect of electrolytes (1-3 *M*) on the rate of extraction and absorbance of ternary complex was observed. The ternary complex in the organic phase may be formulated as Fe.OAm.$(X)_2$, where X=SCN^- or N_3^-, on the basis of the stoichiometry obtained by the curve fitting method[15].

The overall reaction can be expressed as follows:



$$Fe^{3+} + 2X^- + HOAm_o \rightleftharpoons [Fe.OAm.(X)_2]_o + H^+$$

where, $X^- = SCN^-$ or N_3^-
HOAm = hydroxyamidine
o = organic phase.

Effect of diverse ions: The effect of diverse ions in the determination of iron(III) was studied as described in the recommended procedure. The ions chloride, bromide, nitrate, sulphate, borate, urea, thiourea, lanthanoid, alkali and alkaline earth elements, did not interfere in the determination of iron as thiocyanato or azido mixed-complex. The tolerance limits in ppm of other ions in the thiocyanate system, [0.3 *M* HCl, 1.7 ppm Fe(III)] and the azide system, [*p*H=4.5, 3.5 ppm Fe(III)] are shown in parenthesis, in that order: fluoride (400,–); phosphate or arsenate (1200,–); Cu^{2+} (40,–); Zn^{2+} or Cd^{2+} (1000, 800); Fe^{2+} (1000, 800); Ni^{2+} (400, 200); Co^{2+} (400, 200); Mn^{2+} (500, 600); Al^{3+} (400, 400); Cr^{3+} (400, 300); Th^{4+} (200, 200); Ti^{4+} (100, 150); Zr^{4+} (400, 350); Nb^{5+} (40, 60); Ta^{5+} (100, 150); V^{5+} (20, 20); Mo^{6+} (20, 40); W^{6+} (40, 20); U^{6+} (300, 300).

Application of the method to the analysis of drugs — The suggested thiocyanate method was successfull applied to the analysis of tablets or capsule containing ferrous sulphate, ferrous fumarate o ferrous gluconate.

A tablet or a capsule was taken in a Kjeldah flask and heated gently with conc. HNO_3 an H_2SO_4 (10 : 1 v/v) till charring began. Dropwis addition of HNO_3 acid and boiling was continue till colourless liquid was obtained. A few ml o water was added and the solution was evaporate to white fumes. It was then dissolved in a few m of dilute hydrochloric acid and diluted to one litre A 0.5 to 5 ml aliquot of the above solution contain ing ≈ 50 µg iron was taken and iron(III) wa determined by the procedure recommende earlier. The accuracy of results were compare with those obtained by using 1 : 10-phenanthrolin method as shown in Table 2.

TABLE 2—APPLICATION OF THE METHOD TO THE DETERMINATION OF IRON IN DRUGS WITH THIOCYANATE METHOD

Sl No	Drug	Iron	Calculated* from absorbances with 1 : 10-phenanthroline	Calculated* fro absorbances wit hydroxyamidin method
1	Folitrin, Biochem Pharmaceuticals	Ferrous fumarate 0.35 g	0.349 g	0.349 g
2	Foliplex, Kopran Chemicals Co	Ferrous fumarate 0.050 g	0.050 g	0.049 g
3	Calglufer, Sandoz	Ferrous gluconate 0.075 g	0.071 g	0.070 g
4	Redicyte, Merck Sharp & Dohme	Ferrous sulphate 0.3 g	0.28 g	0.28 g

* = An average of 6 determinations.

Acknowledgement

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NOTES

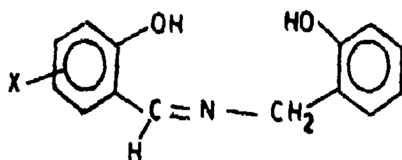
Cobalt(II) Complexes with ONO Donor Tridentate Schiff Bases Derived from Salicylaldehyde, Substituted Salicylaldehydes and Orthohydroxybenzylamine

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THERE has been considerable research interest in recent years in the metal complexes of tridentate dibasic Schiff bases which force the metal (II and III) ions to give dimetallic complexes with novel magnetic properties[1,2]. Most of these studies, however, are concerned with $S=1/2$ systems and little attention has been paid to other spin systems ($S=3/2$, $5/2$). In continuation of our work[1,3] on magnetic exchange properties of dimetallic complexes with $S=1/2$ or $5/2$, we describe here the synthesis of new dimetallic cobalt(II) complexes ($S=3/2$ system) of the Schiff bases (I). The complexes have been characterized on the basis of elemental analysis, conductance, molecular weight, magnetic susceptibility, ir and electronic spectral measurements.



I. X=H, 5-Chloro, 5-Nitro, 5-Bromo, 3-Methoxy, 3-Ethoxy, 3,5-Dichloro, 5,6-Benzo.

Experimental

General method of synthesis of the complexes: Orthohydroxybenzylamine was prepared as described in the literature[4]. The appropriate Schiff base (0.004 mole) was dissolved in 10-15 ml of ethanol by heating on a waterbath. An ethanolic solution of cobalt(II) acetate tetrahydrate (1.08 g; 0.004 mole in 10 ml) was added to the yellow or orange Schiff base solution and the mixture refluxed for 3 hr. The separated precipitates were suction filtered, washed with warm ethanol followed by ether and dried under vacuum. Yield 55%.

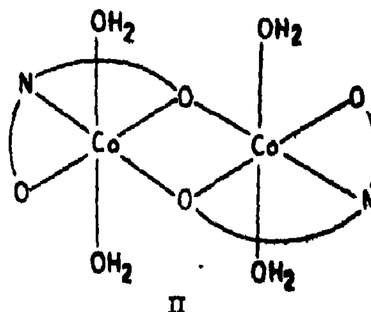
The metal content was determined complexometrically by EDTA using eriochrome black-T an indicator. The electronic absorption spectra were recorded on a Beckman DU-2 spectrophotometer in methanol. Nitrogen analyses, conductance, molecular weight, infrared spectra and magnetic susceptibility measurements were done as reported earlier[5]. The magnetic susceptibilities were corrected for TIP and diamagnetic contributions.

Results and Discussion

The complexes $[Co(OH_2)_2(BBB)]$ (where $BBBH_2$ = Schiff base, I) behave as non-electrolytes in methanol (Λ_M = 3-9 ohm^{-1} cm^2 mole^{-1}). The molecular weight data (Table 1) indicate that the complexes are dimers and they should be formulated as $[Co(OH_2)_2(BBB)]_2$. A shift of the ν(C–O) (phenolic) band of the ligand (~1540 cm^{-1}) to higher energy by $\geqslant$ 10 cm^{-1} on complexation has been used as an unambiguous evidence for the formation of phenolic oxygen bridge in dimetallic complexes[6]. We have also observed such a position shift of the ν(C–O) (phenolic) band indicating the presence of phenolic oxygen bridge. The presence of coordinated water is evident from the occurrence of a medium intense band at around 3200 cm^{-1} in the complexes[7]. The ligands (I) show a band at around 2700 cm^{-1} which is assigned to ν(OH) of the intramolecularly hydrogen bonded OH group. This band is absent in the complexes, indicating the breaking of the hydrogen bonding and consequent deprotonation and coordination to the metal ion. The ν(C=N) stretch occurs at 1630-1660 cm^{-1} in the ir spectra of the ligands and this band undergoes a negative shift in the complexes indicating nitrogen coordination of the azomethine moiety[8].

The complexes exhibit three electronic spectral bands at around 8800, 18000 and 22000 cm^{-1} with molar extinction coefficient (ϵ) in the range 18–24 litre mole^{-1} cm^{-1}. These bands are assigned to the ${}^4T_{1g}(F)\rightarrow{}^4T_{2g}(\nu_1)$, ${}^4T_{1g}(F)\rightarrow{}^4A_{2g}(\nu_2)$ and ${}^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$ transitions respectively in an octahedral field[9]. The low ϵ values are in conformity with the characteristic of O_h symmetry cobalt(II) complexes. The electronic spectral data preclude the presence of a tetrahedral structure[9].

The dimeric nature of these complexes suggests a *μ-bis* (Schiff base) tetraaquodicobalt(II), $[Co(OH_2)_2(Schiff\ base)]_2$ with aquo molecules in the *trans* positions (cf. II) of the two O_h symmetry



II

TABLE 1—ANALYTICAL, MOLECULAR WEIGHT, CONDUCTANCE, MAGNETIC MOMENT, INFRARED AND ELECTRONIC SPECTRAL DATA OF COBALT(II) COMPLEXES OF SCHIFF BASES[a,b]

Complex/Stoichiometry	Found (Calcd.) %Co	%N	Mol. wt Found (Calcd.)	Λ_M ohm^{-1} cm^2 mole^{-1}	ν(C–O) complex (ligand)	ν(C=N) complex (ligand)	μ_{eff} B.M. (Temp.) °K	ν_{max} (ϵ)
$[Co(OH_2)_2(sal\text{-}OHYBA)]_2$ $C_{28}H_{30}O_8N_2Co_2$	18.2 (18.44)	4.0 (4 88)	642 (640)	8.9	1540 (1580)	1615 (1657)	4.70	8730(18), 18180(18), 22470(28)
$[Co(OH_2)_2(5\text{-chlorosal-OHYBA})]_2$ $C_{28}H_{28}O_8N_2Cl_2Co_2$	16 5 (16.64)	3.7 (3 95)	715 (709)	7 8	1530 (1515)	1620 (1660)	5.04	8770(21), 18690(21), 22220(24)
$[Co(OH_2)_2(5\text{-bromosal-OHYBA})]_2$ $C_{28}H_{28}O_8N_2Br_2Co_2$	14 6 (14 79)	3.2 (3.51)	788 (798)	9 8	1535 (1515)	1620 (1655)	5 80	
$[Co(OH_2)_2(5\text{-nitrosal-OHYBA})]_2$ $C_{28}H_{28}O_{12}N_4Co_2$	16 1 (16 16)	7 9 (7.67)	735 (730)	3 4	1540 (1580)	1685 (1640)	5.08	
$[Co(OH_2)_2(3\text{-methoxysal-OHYBA})]_2$ $C_{30}H_{34}O_{10}N_2Co_2$	16 8 (16 86)	4.8 (4 00)	705 (700)	9 6	1530 (1515)	1615 (1640)	4 95	8800(20), 18520(20), 21740(20)
$[Co(OH_2)_2(3\text{-ethoxysal-OHYBA})]_2$ $C_{32}H_{38}O_{10}N_2Co_2$	16 1 (16 21)	3 7 (3.85)	721 (728)	7.5	1540 (1580)	1625 (1660)	4 91	
$[Co(OH_2)_2(3,5\text{-dichlorosal-OHYBA})]_2$ $C_{28}H_{26}O_8N_2Cl_4Co_2$	15 0 (15 17)	3.3 (3 60)	775 (778)	5 5	1530 (1500)	1625 (1640)	4 92	8810(20), 18520(20), 22990(22)
$[Co(OH_2)_2(hydrox\text{-}OHYBA)]_2$ $C_{36}H_{34}O_8N_2Co_2$	15.6 (15 95)	3 5 (3 78)	754 (740)	3 9	1550 (1580)	1610 (1630)	5 24	

(a) Abbreviations sal = salicylaldehyde, 5-chlorosal = 5-chlorosalicylaldehyde, 5-bromosal = 5-bromosalicylaldehyde, 5-nitrosal = 5-nitrosalicylaldehyde, 3-methoxysal = 3-methoxysalicylaldehyde, 3-ethoxysal = 3-ethoxysalicylaldehyde, 3,5-dichlorosal = 3,5-dichlorosalicylaldehyde, hydrox = 2-hydroxy-1-naphthaldehyde and OHYBA = orthohydroxybenzylamine

(b) IR and electronic spectral bands are in cm^{-1}

cobalt(II). The ir data, as discussed earlier, support this structure. The measured magnetic moments (Table 1) of the complexes are in the range 4.70-5.30 B.M. and are characteristic of magnetically dilute octahedral cobalt(II) complexes[9].

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Some Ligational Aspects of Tartrazine : Its Binary and Ternary Lanthanide Complexes

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TARTRAZINE is a basic azo-dye (Acid yellow CI 19140) used for dyeing food-stuffs and preservants[1]. It has also been used as a redox indicator[2] and as sodium salt in inks. It shows a yellow to purple colour change with *p*H, which may be used to explore the possibility of its being used as a metallochromic indicator. However, no attempt seems to have been made to study its complexes in solution.

The present work describes its binary complexes with La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+} and ternary complexes with these metal ions using EDTA as a primary ligand.

Experimental

Standard solutions of metal ions were prepared by dissolving their nitrates (Fluka, AG) and oxides in double distilled water and perchloric acid, respectively, and excess of the acid was evaporated. 1 *M* sodium perchlorate (Riedel) solution was used to maintain the ionic strength at 0.2μ. The dye, obtained from I. C. I., India, was further purified by recrystallization. A 0.2 *N* NaOH (Sarabhai M)

TABLE 1—STABILITY CONSTANTS OF Ln-Trzne BINARY AND Ln-EDTA-Trzne TERNARY COMPLEXES AT 25° AND IONIC STRENGTH OF 0.2M($NaClO_4$)

$Trzne^{-}+H^{+}$	$\log K_n^H$			10.40			—
Ln^{3+}	$\log K_{ML}$ [Ln-Trzne]	S_n	S_α	$\log K_{MAL}$ [Ln-EDTA-Trzne]	S_n	S_α	$\log K_{MAL} - \log K_{ML} = \Delta\log K$
La^{3+}	7.34	±0 02	±0.03	5 89	±0.02	±0.02	−1.45
Ce^{3+}	7.44	+0 03	±0 03	6 19	±0.03	±0.04	−1 25
Pr^{3+}	7.54	±0 02	±0.04	6 59	±0 04	±0.06	−0 95
Nd^{3+}	7.69	±0 05	±0.02	7 19	±0 02	±0.05	−0.50
Sm^{3+}	7 99	±0.05	±0 02	7 49	±0 07	±0 02	−0.50
Gd^{3+}	8 03	±0.05	±0 01	7.55	±0 05	±0 02	−0.48

solution was used to titrate the solution sets. The pH values were recorded on a digital pH meter, Elico model LI-120. The usual sets of solutions for binary and ternary complexes were titrated against the alkali solution and the pH values were recorded. The observed pH values were plotted against the volume of alkali solution (Figs. 1 and 2).

Results and Discussion

The values of proton-ligand stability constants ($\log K_n^H$) and metal-ligand stability constants for 1 : 1 binary ($\log K_{ML}$) and 1 : 1 : 1 ternary ($\log K_{MAL}$) complexes, as computed by Irving-Rossotti[8] technique with their $\Delta \log K$ values have been tabulated in Table 1. The standard deviation and the limit of error have been calculated as S_n and S_α, respectively.

It is obvious from Fig. 1 that the ligand curve practically overlaps the acid curve in the lower pH region. Its separation starts after $pH \approx 8.00$ indicating the deprotonation of the phenolic group of the pyrazole ring[4]. The separation of binary complex curve (curves A – E, Fig. 1) after $pH \approx 6.00$ may be attributed to an early release of phenolic proton due to complexation. Only 1 : 1 complexes have been studied. The higher complexes could not be examined due to precipitation of the hydroxo-species.

The system under study for the ternary complexes is of the type $MA + L \rightleftharpoons MAL$ as is clear from the pH-metric curves in Fig 2. The separation of curve MAL from MA occurs at a higher pH indicating the formation of the ternary complex, MAL, whereas the binary complex MA is formed at a much lower pH. Further, theoretical composite curve drawn by adding horizontal distances of the binary complex curves and free ligands, was found nonsuperimposable on the experimental ternary system curve. This confirmed the formation of the ternary complex.

The ternary complexes were found to be less stable than the corresponding binary ML complexes. This may be due to the coulombic repulsion between the binary complex (MA) and the incoming

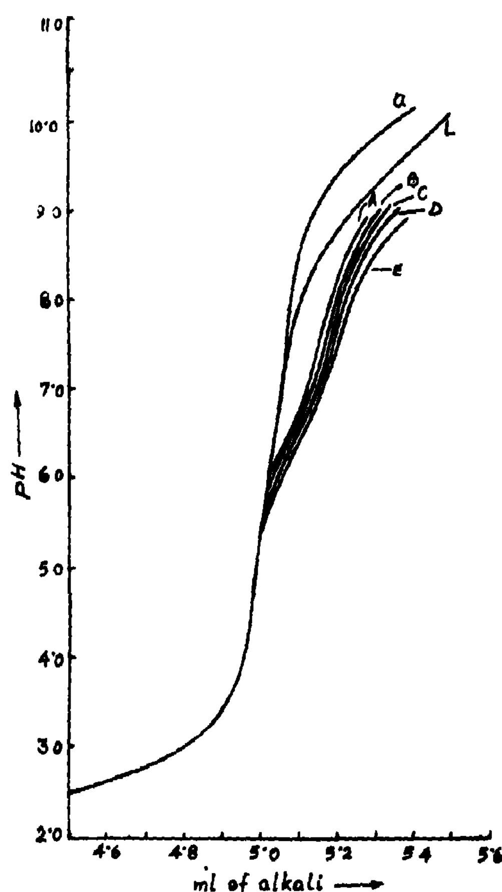



Fig. 1 pH titration curves for binary Ln-Trzne complexes. $A = La^{3+}$, $B = Ce^{3+}$, $C = Pr^{3+}$, $D = Nd^{3+}$, $E = Sm^{3+}$, a = acid curve, L = liquid curve.

ligand L, as shown by the following complexation equations:

$$Ln^{3+} + A^{4-} \rightleftharpoons [LnA]^{-} ; \ [LnA]^{-} + [L]^{-} \rightleftharpoons [LnAL]^{-2}$$

EDTA being a hexadentate ligand, forms a very stable chelate occupying 6 coordination sites. Now, to accomodate a bidentate ligand, water molecules of 7th and 8th coordination sites of the lanthanides may be removed which leaves the geometry of primary complex undisturbed but creates an extra strain on the ternary complex thereby lowering its

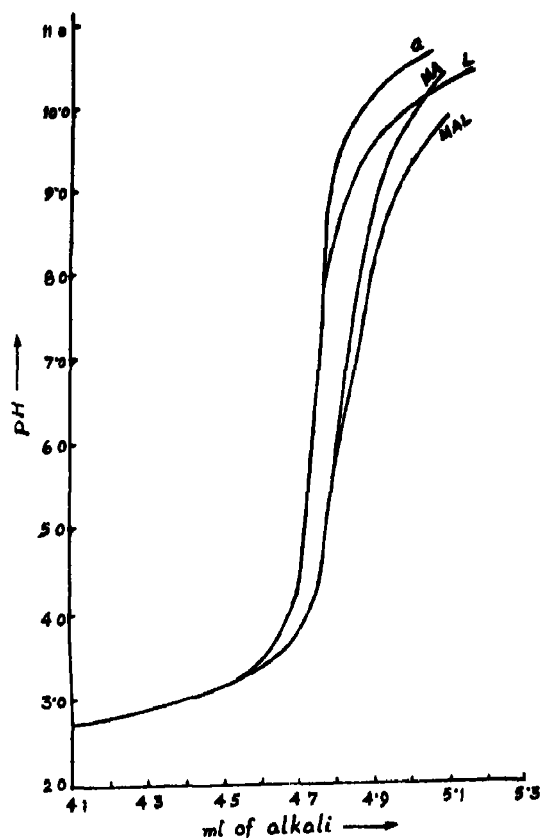


Fig. 2. pH titration curves for the ternary complex La-EDTA-Trzne
a=acid curve, L=ligand curve, MA=binary complex (La-EDTA), MAL=ternary complex

stability. This justifies the negative Δ log K values in the present series.

In case of lanthanides, formation of ionic bonds is generally favoured, because overlap with the metal 4f orbitals is difficult due to the shielding effect of 5s and 5p electrons. This would mean that Born relation $E=Z^2/2r\,(1-1/D)$ should be valid for the complexation equilibrium under study. The stability constants log K_{ML} as well as log K_{MAL} being directly proportional to E, the energy change on complexation of the gaseous metal ion should yield linear plots with Z^2/r (Z is charge and r is radius of the metal ion). In the present case such plots (not shown here) show some deviation from a strict linear nature suggesting partial covalency[8]. Earlier work[8-9] on lanthanide complexes support our observations.

The log-log plots of log K_{MAL} vs log K_{ML} and log K_{MA} have also been examined. The almost linear plots (not shown) indicate that the process of association of L with [Ln-EDTA] species in the ternary system is the same as the association of L or A with Ln^{3+} in corresponding binary systems. A slight variation is observed which may be due to the ligational nature and steric effect of the secondary ligand.

The log K_{ML} and log K_{MAL} values have been correlated with some fundamental properties of lanthanide metal ions, viz., 3rd ionisation potential, charge/size ratio and standard entropies. A linear correlation (not shown) indicates similarity in the nature of complexes. These observations are in agreement with the earlier work[10-11] on lanthanide complexes. The log K_{ML} and log K_{MAL} values have been found to follow the usual trend[12] with respect to the metal ions i.e. $La^{3+}<Ce^{3+}<Pr^{3+}<Nd^{3+}<Sm^{3+}<Gd^{3+}$.

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Determination of Stability Constant of Copper(II) Complexes with Ethylenediamine and Acetyl Salicylate (Aspirinate) by Electrochemical Methods

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A number of studies on mixed ligand complex formation has appeared during the past decade[1-18]

The present investigation deals with the study of mixed ligand complexes of copper(II) with ethylenediamine and aspirinate and evaluation of their formation constants by the method of Schaap

TABLE 1—DERIVED F_{ij} FUNCTION FOR THE Cu(II)-ETHYLENEDIAMINE-ASPIRINATE SYSTEM

$[Cu^{2+}]$=0.5 mM [Aspirinate]=0.2 M μ=1.5   T=298 ± 1°K I_M=100 Div $-E_{1/2}(s)$=0 0165V pH=5.6   A=326 16(Calcd.)

$[X]\times10^{8}$ (moles)	$\log \frac{I_M}{I_C}$	$E_{1/2}$	$F_{00}[X]\times10^{-8}$	$F_{10}[X]\times10^{-14}$	$F_{20}[X]\times10^{-20}$
0.2948	0.0269	0.2345	0 9096	3 0855	1 6468
0.5896	0.0862	0.2455	2 1890	3.7126	1 8870
0 8844	0 0506	0 2524	3 8730	4.3792	2 0117
1 1792	0 0757	0 2570	5.8716	4.9793	2 0177
1.4739	0 0888	0.2610	8 2637	5 6066	2 0398
1 7688	0.0969	0.2644	10 9710	6 2025	2 0366
2.0636	0.1024	0.2675	14 1439	6 8589	2.0613
2.3584	0.1106	0.2700	17 5169	7 4274	2.0468

$B=2.6\times10^{14}$ and $C_{av}=1.968\times10^{20}$.

and McMaster[13]. The formation constants in simple system have been calculated by the method of DeFord and Hume[14] as well as by Mihailov's[15] mathematical method and both the values agree well.

Experimental

All the chemicals used were of reagent grade. The copper solution was prepared from copper sulphate. Sodium salt of aspirin was prepared with sodium hydroxide solution using Toshniwal pH meter. The ionic strength was maintained at 1.5 μ by adding the requisite amount of sodium perchlorate. The polarograms were taken at pH 5.6 adjusted by adding sodium hydroxide and perchloric acid. All the measurements were carried out at 25±1°. Prior to the polarographic examination, purified and pre-saturated nitrogen gas was passed through the test solution (taken in H-type cell) for 20 min to expel dissolved oxygen. All the polarograms were taken on manual polarograph using polyflex spot galvanometer. The d.m.e. with the following characteristics ; m = 1.867 mg/sec, t = 3.5 sec/drop in open circuit, h = 50 cm was used throughout the course of the investigation.

The formation constants of the complexes of copper with ethylenediamine and with aspirinate were measured separately prior to the study of the mixed ligand system. The conditions used corresponded, as closely as possible, to those planned for the mixed systems. In the studies with ethylenediamine, all solutions contained 5×10^{-4} M Cu^{2+} and 0.001% "Triton X-100" as maxima suppressor. The concentration of "free" ethylenediamine (en) was calculated from the pH, and the total amount present from the appropriate pK values[16,17] [pK_1=0.5, pK_2=9.48 for (en) and pK=4.57 for (asp)].

The copper(II)-ethylenediamine-aspirinate system was studied by keeping the concentration of the weaker ligand constant (aspirinate 0.2 M), while varying the concentration of ethylenediamine in each case (0.02-0.16 M).

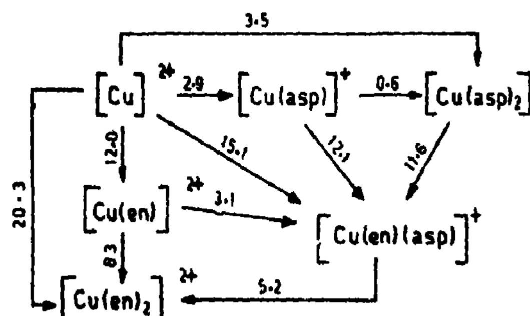
Results and Discussion

Initially, polarograms were run at four different heights and their diffusion controlled nature is confirmed by the nature of the plots of i_d vs $\sqrt{h}$ (h=effective height of mercury column), which were linear and passed through the origin. Again, polarograms were run at four different concentrations and plots of i_d vs concentration were also linear.

The values of formation constants for simple systems have been evaluated by the method of DeFord and Hume as well as by Mihailov's mathematical method. In all cases a single well defined and diffusion controlled wave with a slope of 32±2 mV was obtained on plotting $E_{d.e.}$ against log $[(i/i_d-i)]$, indicating the reduction to be reversible involving two electrons.

A cathodic shift in half wave potential on addition of ethylenediamine in the solution containing copper (complexed with aspirinate) was observed. The shift, however, is greater in presence of aspirinate than in its absence. This indicates the formation of mixed ligand complex of Cu(II) with ethylenediamine and aspirinate. The polarographic characteristics and F_{ij} functions of mixed Cu(II)-ethylenediamine-aspirinate system at one fixed aspirinate concentration of 0.2 M are summarised in Table 1. In this system Cu(II) forms only one mixed ligand species $[Cu(en)(asp)]^{+}$ with $\beta_{11}=12.95\times10^{14}$.

The equilibria among various complex species in the solution (at 25°) is schematically shown below.



Two main changes expected when we go from a simple (MX) to a ternary complex (MXY), are (i) structural changes (i.e. changes in geometry) and (ii) changes in bond energy and mutual interaction of ligands. The second effect may arise from the effects of solvent and ionic strength (as also from statistical effects), change in bond strength, and steric hindrance due to size of the ligand. In the present study the factors which might most probably affect the stability of these mixed complexes are statistical, electrostatic and steric. From a comparison of the dimensionless disproportionation constant K_s for the following equilibrium it is found that the mixed ligand complex is more stable than what might be expected from purely statistical considerations.



$$2[Cu(en)(asp)]^{+} \rightleftharpoons [Cu(en)_2]^{2+} + [Cu(asp)_2]$$

The enhanced stability might therefore be attributed to factors such as steric and electrostatic.

Acknowledgement

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Polarographic Study of Thorium(IV) and Uranyl(II) Complexes with DL-Ornithine Hydrochloride

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AMINO acids have a wide variety of biological, pharmaceutical and other chemical uses, and have been reported to form complexes with some metals. Hence their importance has grown. The polarographic behaviour of some amino acids and their metal complexes have already been studied by Saxena *et al*[1-3].

This communication reports the polarographic behaviour of uranyl(II) and Th(IV) complexes with DL-ornithine hydrochloride, for which no reference could be found in the literature.

Thorium(IV) reduces irreversibly at d.m.e. in presence of DL-ornithine hydrochloride and produces a diffusion controlled wave. The values of kinetic parameters – transfer coefficient (α) and formal rate constant ($K^{\circ}_{f,h}$) have been determined by Koutecky's method[4] as extended by Meites and Israel[5].

Uranyl(II) reduces reversibly at d.m.e. in presence of DL-ornithine hydrochloride and produces a diffusion controlled wave. The composition and stability constants of the metal complexes have been studied by Lingane method[7].

Experimental

DL-Ornithine hydrochloride (DOH) was supplied by B. D. H. Chemicals Ltd., Poole, England and all other chemicals used were of AnalaR grade. Their solutions were prepared in double distilled conductivity water. Triton-X-100 (0.002 percent) was used as maxima suppressor. The ionic strength was maintained by $NaClO_4$.

Polarographic measurements were made on a Toshniwal polarograph, equipped with thermostated H-cell and saturated calomel electrode. Capillary had the characteristics in 0.1 M $NaClO_4$ at -0.5 volts vs S. C. E. with h_{Hg} value of 40 cm, $m = 2.895$ mg/sec, $t = 2.40$ seconds.

The values of kinetic parameters were determined from the polarograms of the solutions containing 0.1 m M Th^{4+}, 0.1 M $NaClO_4$, 0.002 percent Triton-X-100 and various concentrations of DOH.

Results and Discussion

Uranyl-DOH complex at d.m.e. gives a well defined wave in aqueous medium. Reduction is found to be diffusion controlled one electron

reversible step as evident from the constant value of $i_d/\sqrt{h_{eff}}$ within experimental conditions, and from the values of $E_{3/4}-E_{1/4}$ which were 0.06 ± 0.001 V agreeing with the theoretical value for one electron transfer process.

The cathodic shift in $E_{1/2}$ coupled with decrease in diffusion current (i_d) on increasing ligand concentration from 0.0015 *M* to 0.012 *M*, shows the complex formation. The plot of $\Delta E_{1/2}$ vs $-\log C_x$ results in a straight line. Hence the complex formed consists of only one species. The number of ligand/metal ion, J, has been determined from the slope of the plot of $\Delta E_{1/2}$ vs $-\log C_x$ [Fig. 1(a)] at 25° and is $1.09 \simeq 1.0$. The stability constant of the metal complex has been studied by Lingane method[7]. The intercept of the plot of $\Delta E_{1/2}$ vs $-\log C_x$ [Fig. 1(a)] on the ordinate axis at ($-\log C_x=0$) gives $\left(\frac{0.0591}{n}\right)\log K_c$ from which $\log K_c$ is found to be 3.672.

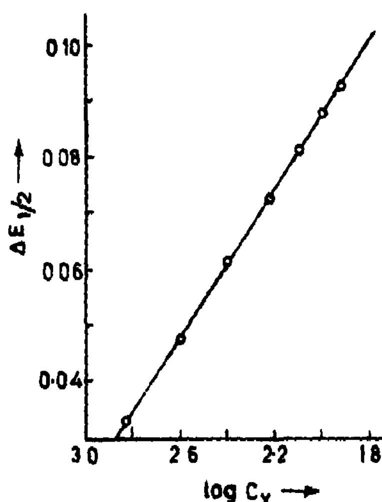


Fig 1(a). Plot of $\Delta E_{1/2}$ vs $-\log C_x$ for UO_2^{2+}-DOH system.

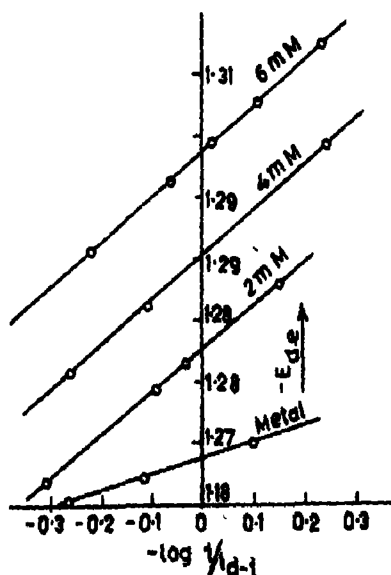


Fig. 1(b). Plot of $\log i/i_d - i$ vs $-E_{d.e.}$ at different concentrations of DOH.

The plots of $\log (i/i_d-i)$ vs $-E_{d.e.}$ [Fig. 1(b)] for Th^{4+} in DOH were linear but their slopes were not in agreement with the theoretical values for reversible wave, indicating the irreversible nature of the waves. The plots of i_d vs $\sqrt{h_{eff}}$ are linear indicating the diffusion controlled nature of the waves. With increase in DOH concentration, the $E_{1/2}$ shifts towards more negative potential showing the complex formation between the metal ion and the ligand, whereas i_d decreases indicating that the aquo-thorium ions differ in size from their complexes with DOH.

The values of kinetic parameters, transfer coefficient (α) and formal rate constant ($K^\circ_{f,h}$), for the electrode reaction have been determined by applying Koutecky's theoretical treatment as extended by Meites and Israel[8]. The kinetic parameters of Th-DOH system in aqueous solution were calculated by using equations (1) and (2)

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n}\log i/(i_d-i) \qquad (1)$$

where

$$E_{1/2} = 0.2412 + \frac{0.05915}{\alpha n}\log\frac{1.349\,K^\circ_{f,h}\,t^{1/2}}{D_0^{1/2}} \qquad (2)$$

($E_{d.e.}$ and $E_{1/2}$ are referred to S. C. E.)

The value of αn was obtained from slope $-\frac{0.05412}{\alpha n}$ of the straight line of $E_{d.e.}$ vs $\log (i/i_d-i)$ [Fig. 1(b)]. The intercept of the same plot gave the value of $E_{1/2}$, which was used to calculate $K^\circ_{f,h}$ at different concentrations of the ligand (Table 1). Since 't' does not vary appreciably over the range of potential covered by the rising part of the curve due to the complexed Th^{4+} ion, it was not considered necessary to apply the correction for t[8].

Table 1—Values of i_d, $E_{1/2}$, αn and $K^\circ_{f,h}$ for Th^{4+}-DOH System at Various Concentrations of DOH at 25° [Fig. 1(b)]

Concn of ligand m*M*	i_d μA	$-E_{1/2}$ (volts)	$D_0\times10^6$	αn	$K^\circ_{f,h}\times10^{10}$ cm/sec
2	1.3	−1.285	5.193	0.7528	0.648
4	1.2	−1.290	4.426	0.7288	1.800
6	1.2	−1.297	4.426	0.7047	2.844

Table 1 shows that the values of α and $K^\circ_{f,h}$ are affected by the concentration of the ligand because of the change in $E_{1/2}$ and i_d with increase in the concentration of complexing agent.

The half wave potential shifts towards more positive value with increase in temperature (Table 2) [Fig. 1(c)] showing the easier reduction of the complex at higher temperature which is in accordance with the irreversible nature of the electrode processes.

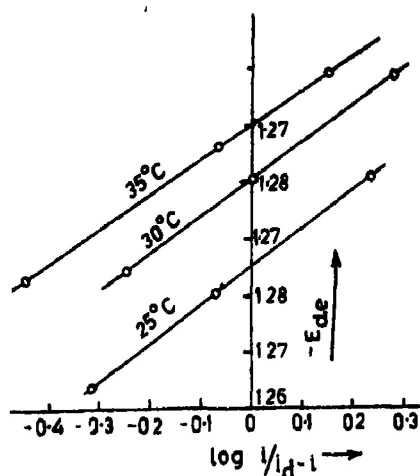


Fig 1(c) Plot of log i/id − i vs − $E_{d.e}$ at different temperatures for Th^{4+}-DOH system.

TABLE 2—VALUES OF i_d, $E_{1/2}$, αn AND $K^0_{f,h}$ FOR Th^{4+}-DOH SYSTEM AT DIFFERENT TEMPERATURES [Fig 1(c)]

Temperature (°C)	i_d μA	$-E_{1/2}$	Temperature coefficient (percent per deg)	$D_0 \times 10^6$	αn	$K^0_{f,h}$ cm/sec
25	1 3	1 285	–	5 193	0 7520	6 118 × 10^{-17}
30	1 5	1 280	2 865	6 915	0 8130	7 109 × 10^{-18}
35	1 7	1 270	3 683	8 980	0 9173	1 927 × 10^{-19}

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Kinetics of Oxidation of Substituted Benzaldehydes by $KMnO_4$ in Buffer Medium

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IN our earlier paper[1] we reported on the kinetics of oxidation of *p*-nitro benzaldehydes by permanganate. We have extended the work on kinetics of oxidation of substituted benzaldehydes by permanganate in buffer medium to various substituted benzaldehydes namely *o*-Cl, *o*-CH_3, *o*-NO_2, *m*-CH_3, *m*-NO_2, 2,4-dichloro, 2,6-dichloro and 2,4-dinitro. An attempt has also been made to verify the general acid catalysis, relative rate of buffer activity with the same substrate, substituent effect, order of reactivity for isomeric benzaldehydes, evaluation of kinetic parameters, steric effects and quantitative calculation of steric interaction energies.

Results and Discussion

Wiberg[2,3] studied oxidation of aromatic aldehydes by $KMnO_4$ in neutral medium and proposed a mechanism. In order to verify the general acid catalysis for the above aldehydes, experiments were carried out at constant *p*H, temperature and ionic strength but at different concentrations of buffer. The buffers selected were pyrophosphate, dihydrogen phosphate and acetate. Other buffers could not be used as they were oxidised by permanganate. The second order rate constants as a function of buffer concentrations are given in Table 1 for *ortho*-nitro compound in three buffers as an example. It was found that increase in buffer concentration increased the rate of reaction for all substrates in three buffers. This confirms that the title reaction undergoes general acid catalysis. To find out the relative rate of buffer activity experiments were done with the same substrate in different buffers under similar conditions. The results given in Table 1 show that the relative rate of buffer activity was found to be pyrophosphate > dihydrogen phosphate > acetate.

TABLE 1—EFFECT OF BUFFER CONCENTRATION ON RATE CONSTANT IN PERMANGANATE-*o*-NO_2 BENZALDEHYDE REACTION

$[RCHO]_0 = 4\,0 \times 10^{-4} M$, $[MnO_4^-]_0 = 5\,0 \times 10^{-4} M$, *p*H = 6.5, $\mu = 0\,2\ M$, Temp. = 35°

$[CH_3COO^-]$	k_2	$[H_2PO_4^-]$	k_2	$[P_2O_7^{4-}]$	k_2
0 20	0 20	0 20	0 28	0 020	0 25
0 15	0 18	0 15	0 24	0.015	0 22
0 10	0 16	0 10	0 19	0 010	0 19
0 05	0 11	0 05	0 15	0 005	0 14
0 01	0 08	0 01	0 10	0 0025	0.12

Units of $k_2 = 1.m^{-1}sec^{-1}$.

The substituent effect on the reaction was studied at constant *p*H, temperature, and buffer concentration for the above substituted benzaldehydes and the rate constants are given in Table 2. The following substituent effect was observed in dihydrogen phosphate buffer of 0.01 *M* at 25° when *p*H is 6.5.

p-NO_2 > *m*-NO_2 > H > *p*-CH_3 > *m*-CH_3 > *o*-NO_2 > *m*-Cl > *o*-Cl > *o*-CH_3. It was found from the substituent effect that electron withdrawing substituents enhance the rate of reaction while electron donating substituents reduce it. The order of reactivity for a given isomeric benzaldehydes was *para* > *meta* > *ortho*. This shows that *ortho* compounds are slower

TABLE 2—RATE CONSTANTS AND KINETIC PARAMETERS FOR THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY PERMANGANATE IN $H_2PO_4^-$ BUFFER AT 35°

Substituent	k_2 l $mol^{-1}sec^{-1}$	$\Delta H^{\neq}$ K cals/mole	$-\Delta S^{\neq}$ Cals/degree
p-NO_2	0.302	6.72	39 3
m-NO_2	0.261	9.01	32 1
m-CH_3	0.108	11 04	26 8
p-CH_3	0.125	10 44	31 0
o-NO_2	0 104	12.22	28 0
m-Cl	0.088	8 54	35 9
o-Cl	0 081	6.72	41 8
2,6-Cl_2	0.062	7 17	40 9
o-CH_3	0.067	8.53	36 5
2,4-Cl_2	0 032	5 15	49 1
2,4-$(NO_2)_2$	0 107	10.40	29 3
*–H	0 224	—	—

* Values taken from reference 2

in oxidation than *para* ones. In other words steric effect of substituent near the reaction centre retards the rate of reaction. The lower kinetic rate observed for *ortho* isomer compared to *para* isomer is due to intramolecular hydrogen bonding leading to formation of a stable five or six membered ring. The other reason for *ortho* compounds reacting at a lower rate compared to *para* or *meta* isomers may be the presence of the bulky group near the reaction site In case of *o*-nitro benzaldehyde intramolecular hydrogen bonding leads to the formation of a six membered ring whereas with *o*-chloro compound a five membered ring may be formed which is usually stable. This makes it difficult for C–H bond to break and hence the lower kinetic rate in the case of *ortho* compounds. In case of *o*-methyl, the bulky nature of substituent retards the rate. The same effect was also confirmed using 2,6-dichloro compound which is much slower than the *o*-chloro compound. The rate constant for unsubstituted, *o*-chloro and 2,6-dichloro benzaldehyde in dihydrogen phosphate buffer at 25° are 0.224, 0.040 and 0.024 $l.m^{-1}$ sec^{-1}, respectively. This type of steric effect retarding the rate of reaction was observed by Jayaraman[4] in the oxidation of benzaldehydes by Cr(VI).

The oxidation was studied in the temperature range from 30 to 50° for all aldehydes in 0.01 *M* dihydrogen phosphate buffer at *p*H 6 5. The second order rate constants at 35° and kinetic parameters are given in Table 2. The free energy of activation is of the order 19.6 K. cals/mole for all substituents. A linear isokinetic plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ shows that all substituted benzaldehydes undergo the same type of mechanism in the buffer medium. The isokinetic temperature was calculated as 275°K from the isokinetic plot.

Evaluation of steric effects: The steric effects due to *ortho* substituents have been evaluated using the linear steric energy relationship[5]

$$\log (k_{ortho}/k_{unsubs.}) = \delta\, E_s$$

where δ is reaction constant, giving the susceptibility of a reaction series to steric effects of substituents. δ depends only upon the nature of the reaction series and is independent of the substituent groups. E_s is steric substituent constant. log $(k_{ortho}/k_{unsub.})$ measures nearly quantitatively the total steric effect of a given substituent relative to the standard substituent, namely methyl group or unsubstituted compound. The positive δ values indicate that the steric requirements of substituents are greater in the transition state than in the initial state.

The negative δ values showed that the substituents of increasing size cause rates to be facilitated as a result of greater steric requirements of the substituents in the reactant than in the transition state.

The steric interaction energy[6] has been calculated using the expression[7,8] $\Delta(\Delta G_s) = -2.303\, RT(\delta\, E_s)$. The values of δE_s and $\Delta(\Delta G_s)$ are given in Table 3 for o-NO_2, o-Cl and o-CH_3 benzaldehydes in buffer medium. All the *ortho* compounds are slower in

TABLE 3—VALUES OF RATE CONSTANTS (k_2), δE_s AND $\Delta(\Delta G_s)$ FOR *ortho* COMPOUNDS IN PERMANGANATE OXIDATION

Property	$-NO_2$	$-Cl$	$-CH_3$
k_2 l $m^{-1}sec^{-1}$	0 05	0 04	0 038
δE_s	−0 51	−0 61	−0.72
$\Delta(\Delta G_s)$(K cals/mole)	0.69	0 83	0.98

rate than unsubstituted because of steric effect of substituent near the reaction centre. As is seen from results in Table 3, the values of δE_s decrease as one proceeds from nitro, chloro to methyl indicating that rate constants should decrease in that order. Similarly, it is seen that the $\Delta(\Delta G_s)$ values are increasing suggesting that the rate constants should decrease in that order. This can be seen from Table 3, where the rate constants for o-NO_2, o-Cl and o-CH_3 are given.

Acknowledgement

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Influence of Some Ionic and Non-Ionic Surfactants on the Electrode Reactions of Ga(III), In(III) and Ge(IV)

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IN continuation of our earlier reports[1-3] on the influence of increasing concentrations of surfactants on the polarographic behaviour of Ni(II), Co(II), Zn(II), Mn(II) and UO_2(II), we now report our studies on the influence of increasing concentrations of some ionic and non-ionic surfactants, viz., lauryl pyridinium chloride (LPC), cetyl pyridinium chloride (CPC), cetyldimethyl benzyl ammonium chloride (CDBAC), sodium lauryl sulphate (SLS), dodecyl benzene sulphonate (DBS), dioctyl sodium sulphosuccinate (DSSS), ethyl digol, Triton X-100 and gelatin on the electrode reactions of Ga(III), In(III) and Ge(IV).

Experimental

Stock solutions of $Ga(NO_3)_3 \cdot H_2O$ (Fluka, A.R.), GeO_2 (Fluka, A.R.) and $In(NO_3)_3 \cdot 3H_2O$(E. Merck, G.R.) were prepared in conductivity water. The concentration of each of the depolarizers in the final solution to be polarographed was maintained at $1 \times 10^{-3}M$. All the surfactants were of high purity and used in their aqueous solutions. A manual polarograph (Toshniwal CL 02) in conjunction with a polyflex galvanometer (Toshniwal PL 50) was used. Purified nitrogen was used for removing dissolved oxygen. The potentials were measured against a saturated calomel electrode (S.C.E.). $NaClO_4$ (0.1 *M*) was used as a supporting electrolyte for Ga(III) and Ge(IV) while 0.1 *M* KCl was used for In(III). Observations were taken at a constant temperature, 25 ± 0.1°. The d.m.e. had the following capillary characteristics (in 0.1 *M* $NaClO_4$, open circuit) m = 1.89 mg/sec, t = 3.1 sec; $m^{2/3} t^{1/6} = 1.84$ mg$^{2/3}$ sec$^{-1/2}$; $h_{corr.} = 72.2$ cm.

The number of electrons (n) involved in the electroreduction of each of the depolarizers was determined by millicoulometric method[4] and was found to be 3 for Ga(III) and In(III) and 4 for Ge(IV). Knowing the value of n, the diffusion coefficient (D) of the depolarizers was calculated by Ilkovic equation at different concentrations of the surfactants. The kinetic parameters (αn_a and $k^o_{f,h}$) were calculated by Koutecky's method[5,6]. Throughout the measurements, the current at the end of the drop (i.e., the maximum current) was recorded, as according to Meites[10] maximum current should be measured if the kinetic parameters for an irreversible wave are to be calculated by Koutecky's method.

Results and Discussion

In the absence of surfactants, both Ga(III) and Ge(IV) yield polarographic maxima under the chosen experimental conditions but In(III) does not produce a maximum. The influence of increasing concentrations of ionic and non-ionic surfactants on the electrode reactions of Ga(III) and Ge(IV) has been studied beyond the stage where the maxima get just suppressed. The concentrations of the surfactants required for the just suppression of the maxima were for Ga(III): [LPC] = [CPC] = [CDBAC] = 1×10^{-3}%, [SLS] = 4.0×10^{-4}%, [DBS] = [DSSS] = 1.6×10^{-3}%, [Triton X-100] = [gelatin] = 1.0×10^{-3}%; for Ge(IV): [LPC] = [CPC] = 2.0×10^{-4}%, [CDBAC] = 5.0×10^{-4}%, [SLS] = [DBS] = [DSSS] = 2.0×10^{-4}%, [ethyl digol] = 0.2%, [Triton X-100] = 1.0×10^{-3}%. The wave-heights are diffusion-controlled in each case in the presence of increasing concentrations of the surfactants as shown by the linearity of i_d vs $h^{1/2}_{corr}$ plots and their passing through the origin.

Irreversibility of the electrode reactions: The various tests of irreversibility[7-9] indicate that the electrode reactions of Ga(III) and Ge(IV) are totally irreversible in the presence of increasing concentrations of ionic and non-ionic surfactants. However, the nature of the electrode reaction of In(III) is different. In 0.1 *M* KCl, In(III) gives a well-defined wave (without any maximum) whose slope (21.4 mV) corresponds closely to a reversible 3-electron reduction. This observation is supported by the reference given in the literature[10]. But on addition of increasing concentrations ($\geqslant 1 \times 10^{-3}$% in the case of anionic and non-ionic and $\geqslant 3 \times 10^{-3}$% in the case of cationic) of the surfactants the electrode reaction of In(III) becomes totally irreversible.

Influence of increasing concentrations of ionic and non-ionic surfactants on the kinetics of the electrode reactions of Ga(III), In(III) and Ge(IV):

(i) *Electrode reactions of Ga(III) and Ge(IV)*: The values of kinetic parameters (αn_a and $k^o_{f,h}$) have been calculated as a function of the concentration of surfactants. The concentration variation was from 2×10^{-4}% to 8×10^{-3}%. A perusal of these values shows that both αn_a and $k^o_{f,h}$ decrease as the concentration of the surfactant is gradually increased beyond the stage where the maxima get just suppressed. A decrease in the values of these parameters shows[11] that the irreversible electrode reactions of Ga(III) and Ge(IV) become more so on adding increasing amounts of ionic and non-ionic surfactants. This conclusion is supported by a decrease in i_d and a negative shift in $E_{1/2}$. These effects indicate inhibition[12] of the electrode processes of Ga(III) and Ge(IV) in the presence of increasing amounts of surfactants.

(ii) *Electrode reaction of In(III)*: As already mentioned, the electrode reaction of In(III) in 0.1 *M* KCl and in the absence of a surfactant is reversible. But on the addition of cationic surfactants the electrode reaction tends towards irreversibility and becomes totally irreversible at [cationic surfactant] $\geqslant 3 \times 10^{-3}$%. On the other hand the

addition of both anionic and non-ionic surfactants even at a lower concentration ($\geq 1 \times 10^{-8}\%$) renders the electrode reaction of In(III) totally irreversible. The values of αn_a and $k^0_{f,h}$ have been calculated at the concentrations of ionic and non-ionic surfactants where the electrode reaction of In(III) becomes totally irreversible and thereafter the influence of increasing concentrations of the surfactants on the values of the kinetic parameters has been studied. A perusal of these values shows that both αn_a and $k^0_{f,h}$ decrease with increasing concentrations of the surfactants. It follows from this that the reversible electrode reaction of In(III) in 0.1 *M* KCl tends towards irreversibility on the addition of ionic and non-ionic surfactants and that the electrode reaction becomes more irreversible with the addition of increasing concentrations of the surfactants. This is further supported by a decrease in i_d and a negative shift in $E_{1/2}$ in the presence of increasing concentrations of the surfactants. The decrease in i_d and a negative shift in $E_{1/2}$ with increasing concentrations of surfactants indicate[13] inhibition of the electrode process of the depolarizers. This may be due to an increase in surface-coverage of the dropping mercury electrode[14].

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Syntheses of 2-Hydroxyisocarbostyrils

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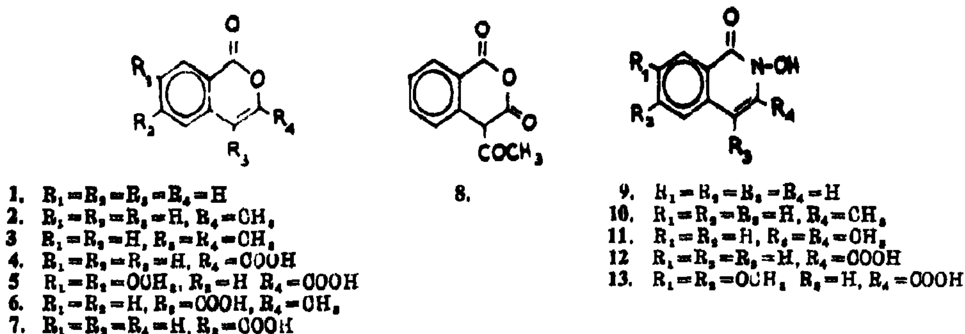
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AS 7-hydroxyisocarbostyrils are effective antidepressant and powerful tranquiliser[1], a convenient synthesis of this class of compounds is desirable. We reported[2] earlier the synthesis of 2-hydroxyisocarbostyrils by nitrosation of indan-1-ones and 3-alkyl(aryl)indan-1-ones with butyl nitrite in presence of sodium methoxide. Similar transformations of 2-alkylindan-1-ones have been described by Moriconi and coworkers[3,4]. Earlier, indeno(3' . 2'-3 : 4)isocoumarin was converted into 2-hydroxyindeno(3' : 2'-3 : 4)isocarbostyril by the action of hydroxylamine[5]. We now report a synthesis of 2-hydroxyisocarbostyrils by the action of hydroxylamine hydrochloride on 4-acetylisochroman-1,3-dione, isocoumarins and isocoumarincarboxylic acids separately in the presence of pyridine.

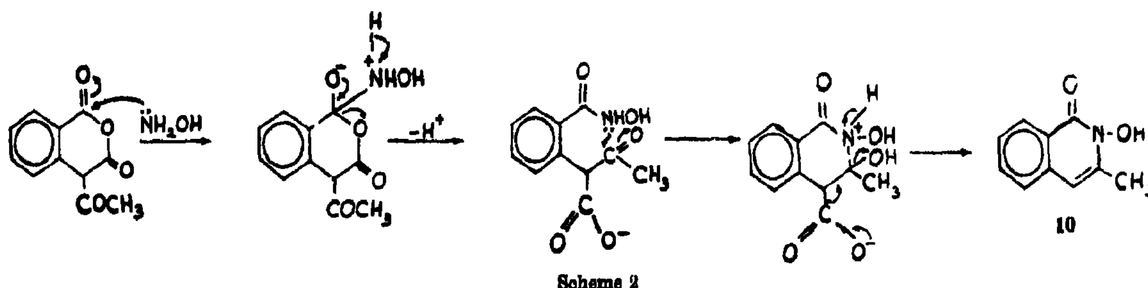
2-Hydroxyisocarbostyrils (**9** to **13**) were obtained by heating isocoumarins (**1** to **5**), respectively, with hydroxylamine hydrochloride in presence of pyridine. Similar experiments on 3-methylisocoumarin-4-carboxylic acid (**6**) resulted in the formation of 2-hydroxy-3-methylisocoumarin (**10**) with decarboxylation, which was characterised by the preparation of its acetate and benzoate derivatives (Scheme 1) The pmr spectrum of **10** showed resonances at δ 2.58 (s, 3H, CH_3), 6.55 (broad s, 1H, vinyl), 8.5 (m, 3H, C-8 peri proton), 7.38-7.74 (m, 3H, aromatic) and 10.25 (broad, 1H, NO*H* exchangeable with D_2O). The ir spectrum of the same compound showed absorptions at 1640 cm^{-1}.

10 was also obtained from similar experiments on 4-acetylisochroman-1,3-dione (**8**). This transformation obviously involves a rearrangement and decarboxylation, which presumably follows the mechanistic course as in Scheme 2.

While this work was almost complete, we noticed a recent publication of Usgaonkar *et al*[6] who reported similar conversion of 3-alkyl (Me, Et, Pr)-7-hydroxyisocoumarins and 3-alkyl (Me, Et, Pr)-7-hydroxyisocoumarin-4-carboxylic acids with hydroxylamine in presence of aqueous sodium carbonate. It is interesting to note that they obtained 3-alkyl(Me, Et, Pr)-2,7-dihydroxy-4-carboxyisocarbostyrils from the 4-acyl(MeCO, EtCO, PrCO)-7-hydroxyisochroman-1,3-diones while in our case we isolated the decarboxylated products from analogous experiments. The mechanism proposed by them (attack of hydroxylamine on acyl carbonyl group) does not seem to be tenable under the experimental conditions adopted by us.

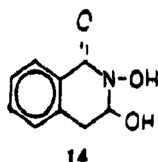


Scheme 1



Scheme 2

The reaction of isocoumarin-4-carboxylic acid (7) with hydroxylamine gave a different result. A compound, m.p. 258-59°, was obtained as the sole product which gave magenta ferric reaction and



showed ir absorption at 1635 cm^{-1}. On the basis of the presence of pmr signals at δ 2.51, 3.42 (OH, exchangeable with D_2O), 3.84 and 10.5 (NOH, exchangeable with D_2O) in the integral ratio of 1 : 1 2 : 1, elemental analysis (molecular composition $C_9H_9O_3N$) and ir data, we tentatively suggest the carbinol structure (14) for the compound.

Table 1—Physical Data of Compounds* 9, 11, 12 and 13

Starting compound	Product	m p (°C)	Yield (%)	IR values (cm⁻¹)
1[9]	9	186-87 (reported[12] 184-85 5)	70	1630
3[10]	11	204-205	60	1630
4[9]	12	227-28	70	1690 1620
5[11]	13	215-16	65	1685 1610

* All the compounds gave satisfactory analysis for carbon and hydrogen

Experimental

All melting points are uncorrected. The ir spectra were recorded on a Perkin-Elmer spectrophotometer, model 577. The pmr spectra were recorded on Varian A-60.

2-Hydroxy-3-methylisocarbostyril (10) :

Method A. From 3-methylisocoumarin (2). A solution of 2 (500 mg) in pyridine (1 ml) was heated with hydroxylamine hydrochloride on a boiling water bath for 2 hr. The mixture was then cooled and cold hydrochloric acid (30 ml ; 2 *N*) was added to it whereby compound (10) separated as solid which was filtered, washed with cold water, dilute hydrochloric acid and water, respectively, and crystallised from acetone as white plates (350 mg), m.p. 172-73° (lit.[8] m.p. 172.5-73°); (Found : C, 68.4 ; H, 5.4. $C_{10}H_9O_2N$ requires C, 68.6 ; H, 5.2%). IR (KBr) : 1640 cm^{-1} (lactam carbonyl) ; pmr ($CDCl_3$) δ 2.58 (s, 3H, CH_3), 6.55 (slightly broad s, 1H, vinyl), 7.38-7.74 (m, 3H aromatic), 8.5 (m, 1H, C-8 peri aromatic proton) and 10.25 (broad s, 1H, NOH, exchangeable with D_2O).

The acetate derivative crystallised from benzene in colourless needles, m.p. 128-29° (Found C, 66.2 ; H, 5.3. $C_{12}H_{11}O_3N$ requires C, 66.4 ; H, 5.1%). IR (KBr) : 1780 (ester carbonyl) and 1660 cm^{-1} (lactam carbonyl).

The benzoate derivative crystallised from benzene as colourless needles, m.p. 168° (lit.[8] m.p. 167-68°) (Found : C, 72.9 ; H, 4.8. $C_{17}H_{13}O_3N$ requires C, 73.1 ; H, 4.7%).

Compounds (9) and (11 to 13) were prepared in an analogous manner from the related isocoumarins (1) and (3 to 5), respectively.

Method B. From 4-acetylisochroman-1,3-dione (**8**) : A solution of **8**[7] (400 mg) in pyridine (1 ml) was heated with hydroxylamine hydrochloride (300 mg) on a boiling water bath for 4 hr. The reaction mixture was then worked up in the same manner as described in method A to afford compound (**10**) which crystallised from dilute acetone as white plates (250 mg), m.p. and m.m.p. 172-73°.

Method C. From 4-carboxy-3-methylisocoumarin (**6**) : 4-Carboxy-3-methylisocoumarin (**6**)[7] was similarly treated with hydroxylamine hydrochloride for 4 hr to afford the same isocarbostyril (**10**), m.p. and m.m.p. 172-73°, yield 60%.

2,3-Dihydroxy-3,4-dihydroisocarbostyril (**14**) : A solution of **7**[8] (400 mg) in pyridine (1 ml) was heated with hydroxylamine hydrochloride (300 mg) on a boiling water bath for 4 hr. The mixture was then cooled, poured into cold hydrochloric acid to afford (**14**) as solid which crystallised from ethanol as colourless needles (250 mg), m.p. 258-59° (Found : C, 60.1 ; H, 5.2 $C_9H_9O_3N$ requires C, 60.3 ; H, 5.0%). IR (KBr) . 1635 cm^{-1} (lactam carbonyl).

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Studies in Heterocyclic Compounds. Part-XXXI : Synthesis of Some 4-Methyl-5-(methyl/*p*-methylphenyl)-5-(arylazo/N-substituted *p*-sulphamylbenzeneazo)-pyrimidin-2-ols as Potential Antibacterials

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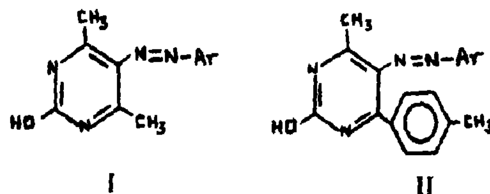
PYRIMIDINE nucleus has been employed as a basis for the synthesis of chemotherapeutic agents and some of its derivatives have been reported to possess antitumor[1], antimalarial[2], diuretic[3], anti-inflammatory, analgesic and antipyretic[4], antimycotic[5], antileukemic[6] and antithyroid[7] activities.

Certain arylazopyrimidines having polar groups like amino and hydroxyl at positions 2,4 and 6 have been reported to possess antibacterial[8], antifolic acid and antineoplastic activity[10]

Although pyrimidinesulphonamides and 5-arylazopyrimidines are reported to be biologically active, hardly any work is reported in literature on the synthesis and study of biological properties of pyrimidines having sulphonamide moiety attached through an azo linkage[11].

Keeping this in view, we have synthesised 4-methyl-6-(methyl/*p*-methylphenyl)-5-(arylazo/N-substituted *p*-sulphamylbenzeneazo)pyrimidin-2-ols of the type I (a,b) and II (a,b) by coupling 4,6-dimethyl- and 4-methyl-6-(*p*-methylphenyl)pyrimidin-2-ols with diazotised simple and sulphonamide bases and the results are reported here. All the synthesised compounds were subjected to *in vitro* screening against *S. aureus*, *E. coli* and *P. pyocyanea* at concentrations of 100 μg/ml and 50 μg/ml.

This work has provided an opportunity to study (i) the effect of various groups present at positions 2,4 and 6 of the pyrimidine ring on the rate of coupling reactions and biological properties against different organisms and (ii) to make a comparison of the antibacterial properties amongst the arylazo and their sulphonamide analogues



a Ar=C_6H_4R
b Ar=$C_6H_4SO_2NHR$

Experimental

4,6-Dimethylpyrimidin-2-ol was synthesised as reported by Klotzer[12].

*4-Methyl-6-(*p*-methylphenyl)pyrimidin-2-ol* : 1-Methyl-3-(*p*-methylphenyl)propane-1,3-dione (22 g ; 0.125 mol) and urea (7.5 g ; 0.125 mol) were taken together in a R. B. flask (500 ml), ethanol (60 ml) was added and the contents refluxed on a water bath for about an hour. Concentrated hydrochloric acid (17 ml) was then added dropwise, the contents further refluxed for an hour and left overnight. The hydrochloride of 4-methyl-6-(*p*-methylphenyl)pyrimidin-2-ol which separated out as shining light brown needles was filtered, dissolved in minimum quantity of water and neutralized with aqueous sodium hydroxide (10%) when 4-methyl-6-(*p*-methylphenyl)pyrimidin-2-ol separated out as yellow crystalline needless, m.p. 239°, yield 12.5 g, 50% (Found : C, 71.6 ; H, 5.9.

$C_{13}H_{12}N_2O$ requires C, 72.0; H, 6.0%) IR: ν_{max}^{KBr} cm^{-1} . 1575 (C=C), 1613 (C=N), 3333 (O–H stretching), 1190 (O–H bending), 2778 (C–H stretching), 1390 (C–O stretching).

4,6-Dimethyl-5-(arylazo)pyrimidin-2-ol : To a well cooled and stirred solution of 4,6-dimethyl pyrimidin-2-ol (0.31 g; 0.0025 mol) in ethanol containing sodium hydroxide (10 ml; 1 *N*) was gradually added a diazotised solution of base (0.0025 mol). 4,6-Dimethyl-5-(arylazo)pyrimidin-2-ol, which separated out on acidification and dilution with water, was crystallised either from ethanol or DMF-ethanol or GAA-ethanol mixture as a coloured solid.

Similar set of reaction was carried out with 4-methyl-6-(*p*-methylphenyl)pyrimidin-2-ol to get 4-methyl-6-(*p*-methylphenyl)-5-(arylazo)pyrimidin-2-ol and all the compounds of the two series are recorded in Tables 1 and 3.

TABLE 1—4,6-DIMETHYL-5-(ARYLAZO)PYRIMIDIN-2-OLS
(Ia : $R_1 = R_2 = CH_3$, $Ar = C_6H_4R$)

Sl. No	R	m.p °C	Colour	Yield %	Crystallisation solvent
1.	H	219	BL	46	DMF/EtOH
2.	*o*-Methyl	158	B	39	DMF/EtOH
3	*m*-Methyl	165	B	98	DMF/EtOH
4.	*p*-Methyl	245	BI	41	GAA/EtOH
5	*o*-Chloro	228	B	52	DMF/EtOH
6	*m*-Chloro	225	B	56	DMF/EtOH
7	*p*-Chloro	240	B	58	DMF/EtOH
8	*p*-Bromo	247	B	52	DMF/EtOH
9	*o*-Nitro	241	B	54	Py/EtOH
10	*m*-Nitro	212	B	53	DMF/EtOH
11.	*p*-Nitro	191	B	57	EtOH
12	*o*-Methoxy	300	BL	40	DMF/EtOH
13.	*m*-Methoxy	158	B	39	EtOH
14	*p*-Methoxy	118	B	40	GAA/EtOH
15	2,5-Dichloro	262	BL	60	DMF/EtOH

TABLE 2—4,6-DIMETHYL-5-(N-SUBSTITUTED *p*-SULPHAMYLBENZENEAZO)PYRIMIDIN-2-OLS
(IIa : $R_1 = R_2 = CH_3$, $Ar = C_6H_4SO_2NHR$)

Sl No.	R	m.p °C	Colour	Yield %	Crystallisation solvent
1	Acetyl	252	B	43	DMF/EtOH
2	Phenyl	250	B	38	DMF/EtOH
3	*o*-Methylphenyl	238	B	40	DMF/EtOH
4.	*m*-Methylphenyl	227	BL	42	DMF/EtOH
5	*p*-Methylphenyl	107	B	48	Cyclohexane/ Benzene
6.	*o*-Chlorophenyl	245	BL	15	DMF/EtOH
7.	*m*-Chlorophenyl	236	BL	40	DMF/EtOH
8.	*p*-Chlorophenyl	243	B	45	DMF/EtOH
9	*p*-Nitrophenyl	255	B	58	DMF/EtOH
10.	*o*-Methoxyphenyl	240	B	50	DMF/EtOH
11.	4,6-Dimethyl pyrimidin-2-yl	267	BL	44	DMF/EtOH

4,6-Dimethyl- and 4-methyl-6-(*p*-methylphenyl)-5-(N-substituted *p*-sulphamylbenzeneazo)-pyrimidin-2-ols were similarly synthesised and are recorded in Tables 2 and 4.

TABLE 3—4-METHYL-6-(*p*-METHYLPHENYL)-5-(ARYLAZO)PYRIMIDIN-2-OLS
[Ib : $R_1 = CH_3$; $R_2 = C_6H_4CH_3(p)$; $Ar = C_6H_4R$]

Sl No.	R	m.p. °C	Colour	Yield %	Crystallisation solvent
1.	H	147	RB	38	EtOH
2.	*o*-Methyl	129	B	31	EtOH
3	*m*-Methyl	282	B	31	EtOH
4	*p*-Methyl	223	B	34	GAA/EtOH
5	*m*-Chloro	277	R	44	DMF/EtOH
6	*p*-Chloro	135	B	45	DMF/EtOH
7	*p*-Bromo	266	R	52	DMF/EtOH
8	*o*-Nitro	293	B	48	DMF/EtOH
9	*m*-Nitro	278	R	46	DMF/EtOH
10	*p*-Nitro	297	B	50	DMF/EtOH
11	*o*-Methoxy	217	B	40	DMF/EtOH
12	*m*-Methoxy	156	B	39	DMF/EtOH
13	*p*-Methoxy	264	B	41	DMF/EtOH
14	2,5-Dichloro	127	Y	47	EtOH

TABLE 4—4-METHYL-6-(*p*-METHYLPHENYL)-5-(N-SUBSTITUTED *p*-SULPHAMYLBENZENEAZO)-PYRIMIDIN-2-OLS
[IIb : $R_1 = CH_3$, $R_2 = C_6H_4CH_3(p)$, $Ar = C_6H_4SO_2NHR$]

Sl No	R	m.p °C	Colour	Yield %	Crystallisation solvent
1	H	227	B	52	DMF/EtOH
2	Acetyl	274	B	38	DMF/EtOH
3	Phenyl	122	B	38	EtOH
4	*o*-Methylphenyl	204	R	42	DMF/EtOH
5	*m*-Methylphenyl	205	R	40	DMF/EtOH
6	*p*-Methylphenyl	225	B	42	Py/EtOH
7	*o*-Chlorophenyl	269	R	42	DMF/EtOH
8	*m*-Chlorophenyl	275	R	40	EtOH
9	*p*-Chlorophenyl	172	O	43	GAA/EtOH
10	*o*-Methoxyphenyl	178	R	42	DMF/EtOH
11	Guanidyl	281	RB	44	DMF/EtOH
12	Pyrimidin-2-yl	226	B	46	DMF/EtOH
13.	4,6-Dimethyl pyrimidin-2-yl	253	B	42	DMF/EtOH
14	2,6-Dimethyl pyrimidin-4-yl	277	RB	44	GAA/EtOH
15	4,6-Dimethoxy pyrimidin-2-yl	161	B	45	GAA/EtOH

GAA = Glacial acetic acid , DMF = Dimethyl formamide , Py = Pyridine , B = Brown , O = Orange , R = Red , BL = Black.

All the compounds gave consistent elemental analysis.

During the course of coupling reactions, it was observed that the presence of non-polar groups like alkyl or aryl at positions 4 and 6 retarded the rate of coupling, thereby giving lower yields which was in accordance with the work reported earlier[9] that only polar groups enhanced the rate of coupling reactions. It was also observed that replacement of methyl by *p*-toluyl at position 6 further reduced the rate of coupling, resulting in lower yields and it could be attributed to the steric effect of this bulky group.

The ir spectral studies of 4,6-dimethyl- and 4-methyl-6-(*p*-methylphenyl)-5-(arylazo/N-substituted *p*-sulphamylbenzeneazo)pyrimidin-2-ols revealed the presence of N=N group by absorbing in the region 1535-1567 cm^{-1}. The respective asymmetric and symmetric stretching vibrational modes of

S=O, from sulphonamide group appeared at ~ 1300 cm^{-1} and ~1090 cm^{-1}.

In the nmr spectral studies of 4-6-dimethylpyrimidin-2-ol in DMSO(D_6), the singlets at 2.28, 6.48 and 9.26 δ appeared due to CH_3, pyrimidine ring C–H and O–H protons respectively. However, in case of 4-methyl-6-(*p*-methylphenyl)-pyrimidin-2-ol, two methyl groups attached to pyrimidine ring and benzene ring were characterised by two singlets at 2.15 δ and 2.25 δ respectively; the proton of the pyrimidine ring in this compound was observed at 6.72 δ. The aromatic protons were represented by two doublets centered at 7.2 δ (2H, *ortho* to methyl group) and 7.85 δ (2H, *ortho* to thiazole ring) while the O–H protons by a singlet at 9.2 δ. The absence of singlet at 6.48 δ and 6.72 δ in the coupled products of the two series of compounds confirmed that coupling had taken place.

Antibacterial properties : When screened at 50 μg/ml, 4,6-dimethyl-5-(arylazo)pyrimidin-2-ols exhibited activity of varying degree against all the three micro-organisms and the order of activity was *P. pyocyanea* > *S. aureus* > *E. coli*. On comparing the activities of the different compounds, it was observed that the introduction of methyl group in the arylazo group decreased the activity. However, the replacement of this methyl by an electron withdrawing group like halogen atom or a nitro group caused an enhancement in the activity, particularly against *P. pyocyanea*. Further, the exchange of methyl at position 6 by a toluyl group decreased the activity against *P. pyocyanea* while the activity against *E. coli* increased to a considerable extent, there being no marked effect on *S. aureus*.

Another important observation made in the course of this work was that replacement of the arylazo group by sulphonamido group rendered these compounds less active.

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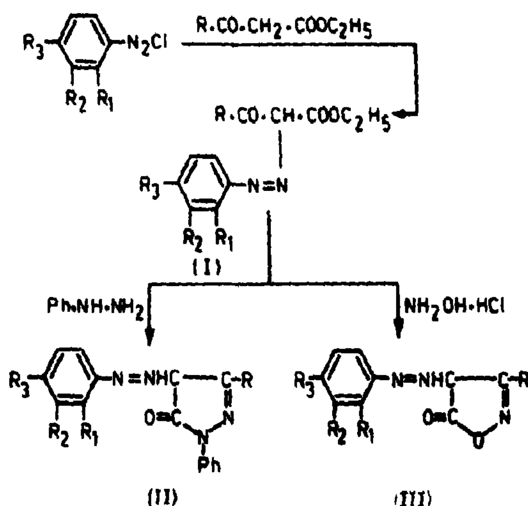
Synthesis of Some New 1-Phenyl-3-methyl/phenyl-4-(*o/m/p*-substituted benzeneazo)-5-pyrazolones, 1-Phenyl-3-(*o/m/p*-substituted anilic)-5-pyrazolones and 3-Methyl/phenyl-4-(*o/m/p*-substituted benzeneazo)-5-isoxazolones as Possible Biological Agents

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EXTENSIVE work on the applications of 5-pyrazolones, isoxazolones and their derivatives in chemotherapy has been reported[1-6]. Pyrazolones have also been used in analytical chemistry[6]. Keeping this in view some substituted benzenediazonium chlorides were coupled with ethyl acetoacetate and ethyl benzoylacetate and subsequent refluxing of the resulting products (I) with phenylhydrazine and hydroxylamine hydrochloride respectively gave the pyrazolones (II) and isoxazolones (III). The reaction, in general, may be represented as follows



Some anilic-5-pyrazolones were also synthesised by condensing malonanilic acids with phenylhydrazine. Purity and homogeneity of all the compounds were checked by tlc and elemental analysis.

Experimental

Melting points recorded are uncorrected. IR spectra were taken in KBr film on a Beckmann IR spectrophotometer. Malonanilic acids required for the work were synthesised by the method of Singhal and Ittyereh[7].

Ethyl-4-bromo-2-methyl benzeneazo acetoacetate (I) : 4-Bromo-2-methyl aniline (1.86 g) was diazotised in the usual manner. The filtered diazonium solution was run slowly into a well cooled mixture of ethyl acetoacetate (1.95 g) in ethanol (2.5 ml) and sodium acetate (10 g) in water (2.5 ml). A

yellow precipitate separated out immediately which was collected after 8 hr and recrystallised from ethanol. ν_{max}^{KBr} : 650 (C–Br), 1620 (–N=N), 2900 ($C-CH_3$), 1020 and 1095 cm^{-1} (1, 2, 4 substitution in benzene ring).

Compounds 1-5 were obtained in the same way.

1-Phenyl-3-methyl-4-(4'-bromo-2'-methyl benzeneazo)-5-pyrazolone (II) : A mixture of 3.27 g of (I) dissolved in glacial acetic acid and phenylhydrazine (1.08 g) was refluxed for 1 hr. Orange-red crystals, obtained on cooling, were recrystallised from glacial acetic acid. ν_{max}^{KBr} : 670 (C–Br), 1640 (C=O cyclic), 1542 (–N=N), 1250 ($N-C_6H_5$), 1460 and 1495 (five membered heterocyclic ring), 995 and 1040 cm^{-1} (1, 2, 4 substitution in benzene ring).

Compounds 6-10 were obtained in the same way.

3-Methyl-4-(4'-bromo-2'-methyl benzeneazo)-5-isoxazolone (III). A mixture of 4.10 g of (I) dissolved in excess ethanol, hydroxylamine hydrochloride (1.0 g) and sodium acetate (5 g) both dissolved in the minimum quantity of water was refluxed for 4 hr. Pale yellow crystals obtained on cooling was recrystallised from ethanol. ν_{max}^{KBr} 605 (C–Br), 1720 (C=O cyclic) ; 1560 (–N=N), 1466 and 1560 (five membered heterocyclic ring), 960 and 1010 cm^{-1} (1, 2, 4 substitution in benzene ring).

Compounds 11-16 were obtained in same way

1-Phenyl-3-(4'-bromo-2'-methyl anilic)-5-pyrazolone A mixture of 2.72 g of malon-4-bromo-2-methyl anilic acid dissolved in ethanol and phenylhydrazine (1.08 g) with 2 drops of conc. H_2SO_4 was refluxed for half an hour. White crystalline product obtained on cooling was recrystallised from ethanol. ν_{max}^{KBr} 610 (C–Br), 1665 (C=O cyclic), 1296 ($N-C_6H_5$), 2830 ($C-CH_3$), 3400 (–NH), 1402 and 1490 cm^{-1} (five membered heterocyclic ring).

Compounds 17-19 were synthesised in the similar manner.

Biological activity Some of the synthesised pyrazolones and isoxazolones were tested for their antibacterial and antifungal activity *in vitro*. The activity of a compound against the organism is indicated within the brackets.

Compound no. (6) against bacteria *E. coli* (+) and fungi *K. leb* ; no. (7) against bacteria *M. tuberculosis* (1.56 r/ml) ; no. (8) against bacteria *M. tuberculosis* ; no. (11) against bacteria *M. tuberculosis* (12.5 r/ml), *E. coli* and fungi *K. leb* ; no. (12) against bacteria *M. tuberculosis* (3.12 r/ml) and the fungi *T. mentagrophytes* (25 r/ml), no. (13) against bacteria *M. tuberculosis* (12.5 r/ml) ; no. (17) against bacteria *M. tuberculosis* (12.5 r/ml), *E. coli* (++) and the fungi *C. albicans* and *K. leb* (++) ; no. (18) against bacteria *M. tuberculosis* (6.25 r/ml), and no (19) against the bacteria *M. tuberculosis* (12.5 r/ml), *E. coli* (++) and the fungi *C. albicans* and *K. leb* (++).

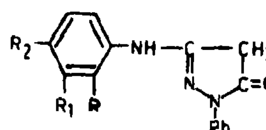
In addition to this, compounds no. (6), (11), (19) were screened for anti-inflammatory activity and no. (7), (9), (10), (14) and (18) for anti-convulsant activity, but none was found active except compound no. (19) which showed some anti-inflammatory activity.

TABLE 1

Sl No	Compounds	R	R_1	R_2	R_3	m p (°C)	Yield (%)
1	I	CH_3	CH_3	H	Br	112	95 71
2	I	CH_3	H	CH_3	Br	72	89.90
3	I	CH_3	Br	H	CH_3	188	85 02
4	I	C_6H_5	CH_3	H	Br	107	86.12
5	I	C_6H_5	Br	H	CH_3	83	77.63
6	II	CH_3	CH_3	H	Br	176	59.80
7	II	CH_3	H	CH_3	Br	185	35 04
8	II	CH_3	Br	H	CH_3	170	70.08
9	II	C_6H_5	CH_3	H	Br	158	51 73
10	II	C_6H_5	Br	H	CH_3	205	49.65
11	III	CH_3	CH_3	H	Br	156	74.32
12	III	CH_3	H	CH_3	Br	180	55 74
13	III	CH_3	Br	H	CH_3	141	64 86
14	III	C_6H_5	CH_3	H	Br	119	50.55
15	III	C_6H_5	H	CH_3	Br	192	34.08
16	III	C_6H_5	Br	H	CH_3	126	41 34

All the compounds gave consistent carbon hydrogen and nitrogen analysis

TABLE 2



Sl No	R	R_1	R_2	m p (°C)	Yield (%)
17	CH_3	H	Br	224	53 48
18	H	CH_3	Br	236	58 14
19	Br	H	CH_3	218	59 59

All the compounds gave consistent carbon, hydrogen and nitrogen analysis

Acknowledgement

The authors are grateful to the Principal, St. John's College, Agra for facilities. Thanks are also due to C. D. R. I., Lucknow for screening the compounds for anti-inflammatory and anti-convulsant activities

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A New Sensitive and Selective Reagent for Extraction of Trace Amount Molybdenum in Iso-Amyl Alcohol and Photometric Determination

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INSPITE of the large number of thio-ligands being utilized in analytical chemistry, a very limited number of thiols as photometric reagents for the determination of molybdenum(VI) is known[1-6]. Solvent extraction studies of coloured chelates formed by Mo(VI) with a few thiols were reported earlier[7-9]. Dithiol has been extensively used in a large number of applications[10-12].

In the present study a mercapto compound, β-mercapto-resorcylic acid, has been employed as a chelating agent for molybdenum for its solvent extraction and photometric determination. The thiol reagent reacts with Mo(VI) to form a stable violet chelate extractable into iso-amyl alcohol. The complex extracted from 2 *M* HCl medium absorbs at 490 nm.

Experimental

A Hilger Uvispek spectrophotometer, with matched 1 cm glass cells, was used for all absorbance measurements.

Reagents and solvents : Ammonium heptamolybdate octahydrate was dissolved in water containing a few drops of ammonia. The metal content of the solution was estimated by oxine method[17]. Solutions of varying strengths were prepared by dilution of the stock. A 0.5% solution of the reagent was prepared by dissolving the β-mercapto-resorcylic acid in double distilled water. Solutions of diverse ions were prepared from their soluble salts and were standardized by conventional procedures. Iso-amyl alcohol (E. Merck, G. R.) was directly used for extraction.

Preparation of β-mercapto-resorcylic acid : The reagent was prepared following the method of Pantletschke and Benger[18]. A 0.5% reagent solution was prepared by dissolving the weighed amount in 100 ml of 0.1 *M* NaOH and warming it for 10 min at 60° under N_2. The solution was neutralised with acetic acid or hydrochloric acid under cold condition. The reagent solution is stable only for 6 hr at room temperature and should be prepared fresh before use.

Extraction procedure : A known amount of molybdenum(VI) solution (50-100 μg/ml) is taken in a 100 ml separatory funnel with 5 ml of 0.5% reagent solution and 5 ml of 6 *M* hydrochloric acid. Water is added to make up the volume of the aqueous phase to 15 ml. The violet molybdenum complex is extracted by shaking for 5 min with 10 ml of iso-amyl alcohol followed by 3×5 ml portions of the solvent. The combined extract is dried over anhydrous sodium sulphate, transfered to a 25 ml volumetric flask and diluted to the mark with iso-amyl alcohol. The absorbance of the complex is measured at 490 nm against a solvent blank.

Procedure for alloy steel : 0.5 g of the steel sample is dissolved in 50 ml of 3 *M* sulphuric acid and the solution digested on a hot plate, with repeated addition of acid, to a syrupy consistency and treated with 5 ml of conc. nitric acid for complete digestion. The solution is evaporated on a hot plate until fumes of sulphur dioxide are evolved. It is diluted with 50 ml of water, boiled and filtered. The filtrate and washings are collected in a 250 ml volumetric flask and made upto the mark. The molybdenum content is determined by the above stated procedure using ascorbic acid as masking agent.

Results and Discussion

Absorption spectrum : The absorption spectrum of the complex (Mo, 4 ppm) extracted from 2 *M* HCl taken in the wavelength region 450-700 nm shows a maximum at 490 (violet) measured against solvent blank. The reagent blank shows no absorption at this wavelength.

Optimum conditions for complex formation : The optimum range of reagent concentrations is 3 to 10 ml of 0.5% reagent solution. 5 ml of the solution was used for each measurement.

The optimum acid concentration for maximum colour development was 1.5-4.5 *M* HCl. Extractions and measurements were made at 2 *M* HCl. Quantitative extraction was achieved with 5 min of shaking. The molybdenum complex was found to be stable in the solvent for 6 hr at room temperature.

Beer's law, optimum range, photometric error and sensitivity : Measurements of absorbances of a series of molybdenum complex extracts containing varied amounts of Mo(VI) were made at 490 nm against the solvent blank. The system adheres to Beer's law from 0.25 to 8 ppm of molybdenum(VI). The optimum range of determination, obtained from Ringbom's plot is 1-5 ppm. The % relative error per 1% absolute photometric error following Ayres' equation is 2.71. The molar absorptivity of the complex and Sandell's sensitivity of the reaction are 1.94×10^4 l. mole^{-1} cm^{-1} and 0.00492 μg cm^{-2} of Mo(VI), respectively.

Composition of the complex : The plot of absorbance against the mole-fraction of the metal M/(M+R) shows a sharp break at 1 : 2 (M : R) composition at 490 nm. The mole ratio plot gives the same composition (1 : 2) with 1.042×10^{-3} *M* metal and reagent solutions.

Degree of dissociation and stepwise and overall stability constants : The degree of dissociation, α, was calculated from Harvey-Manning's equation[16]

TABLE 1—STEPWISE AND OVERALL STABILITY CONSTANTS OF THE MOLYBDENUM COMPLEX (1 : 2) AT 28 ± 1°

Harvey-Manning's method					Leden's method			Yatsimirskii's method		
A_m	A_s	α	C	log K	log K_1	log K_2	log K	log K_1	log K_2	log K
0.812	0.648	0.202	4.169×10^{-5} *M*	10.14	5.01	4.85	9 86	5.16	4.85	10.01

and the instability constant K' was evaluated from the formula $K'=4\alpha^3 C^2/1-\alpha$ for a 1 : 2 complex (C is the total analytical concentration of the complex). The stepwise stability constants K_1 and K_2 were evaluated by Leden's and Yatsimirskii's methods[18,19]. The values are reported in Table 1.

Effect of diverse ions : The tolerance limits for the interfering ions added separately for 4 ppm molybdenum(VI) metal in the final extract were determined at 490 nm. A change of 0.005 absorbance unit at 490 nm was taken as the standard. At 2 *M* HCl acidity 5 times excess of almost all the metal ions excepting W(VI), Re(VII), Fe(III), Pd(II) have been tolerated. Masking with fluoride removed the interference of Fe(III) and tolerance limit increased to 20 ppm. 50 ppm each of sulphate, nitrate, phosphate, citrate, tartrate, fluoride, EDTA, oxalate did not interfere in the determination. The tolerance limits of the interfering ions increased if a higher acidity (3.5 *M* HCl) was maintained for extractions.

Analysis of high-speed steel (BAS 60 b) : A number of determinations were made with the steel solution. Average of several such determinations of the standard steel gave a result of 0.42% Mo (certified value, 0.43% Mo).

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Recent Advances in the Chemistry of Simple and Bimetallic Alkoxides of Later Transition Elements (with particular reference to the '3d' series)*

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After giving a survey of the spurt in the literature during the last 4-5 years on the chemistry of later transition metals in general, a brief account has been presented of the recent work carried out in the author's laboratories on the simple and bimetallic alkoxides of later '3d' metals. The synthesis of a number of simple alkoxides of Cr(III and IV), Mn(II), Fe(II and III), Co(II), Ni(II) and Cu(II) has been described. Except for alkoxides of iron(III), $Fe(OR)_3$ in general and $Cr(OBu^t)_4$, almost all these alkoxides are non-volatile and insoluble in organic solvents. These polymeric alkoxides of later '3d' metals further differ from the alkoxides of earlier transition and main group metals in comparatively much lesser lability of their alkoxy groups. The sharp differences (again observed for the first time in metal alkoxide chemistry) in the alcoholysis reactivity of these alkoxides with changes in ramification of the alkyl group have been correlated with changes in their stereochemistry. Further, a large number of monomeric volatile bimetallic isopropoxides of the above metals with the general formula $M[Al(OPr^i)_4]_n$, have been synthesised. Physico-chemical (spectroscopic and magnetic) properties of these derivatives indicate simple coordinated structures with tetraisopropoxyaluminate moieties functioning as bidentate and in some cases as tridentate ligands.

ALTHOUGH the alkoxide chemistry of non-transition and earlier transition elements has been extensively explored during the last three decades[1], the corresponding derivatives of later transition metals received very little attention[1-3] till recently except for some work on the magnetic and spectroscopic properties of mainly the methoxide derivatives of '3d'[5-9] metals[4]. Further, in contrast to the soluble and volatile alkoxides of earlier transition metals, almost all the alkoxides of later '3d' elements were found to be insoluble with the exception of iron(III) alkoxides[5] and chromium tetra-*t*-butoxides[6]. There appears to be a spurt, particularly during the last 4-5 years, in research activity in a number of laboratories on the alkoxy derivatives of later elements of the first transition series (chromium[7-11], manganese[12-14], cobalt[15,16], nickel[17,18] and copper[19-23]) and of the second and third transition series (molybdenum[24,25], tungsten[26], rhenium[27,28], ruthenium[29], rhodium[30] and platinum[31-35]) including the synthesis of a number of soluble bimetallic[36,37] alkoxides of later '3d' metals. Sterically demanding alcohols have also received special attention[38,39] for enhancing the kinetic stability of transition metal alkoxides in general.

Recent work carried out in our laboratories on the synthesis, interchange reactions, spectroscopic and magnetic properties of the simple alkoxides with the general formulae $Cr(OR)_3$, $Co(OR)_2$, $Ni(OR)_2$ and $Cu(OR)_2$, as well as the bimetallic alkoxides $Cr[Al(OR)_4]_3$, $Mn[Al(OR)_4]_2$, $Fe[Al(OR)_4]_{2\ \&\ 3}$, $Co[Al(OR)_4]_2$, $Ni[Al(OR)_4]_2$ and $Cu[Al(OR)_4]_2$ will now be briefly presented.

Special characteristics of alkoxides of later '3d' transition metals :

Lower alkoxides of earlier transition and main group elements (with the exception of methoxides) are generally volatile and soluble in organic solvents. By contrast, the alkoxides of later '3d' metals [with the exception of ferric and chromium(IV) alkoxides and some highly hindered alkoxides of bivalent chromium[10] and manganese[12]] are non-volatile and insoluble in organic solvents.

Another novel feature of these new alkoxides is their selective reactivity towards other alcohols. In spite of the strength of the metal-oxygen bonds, one of the characteristic features of alkoxides of elements studied so far is their lability due to facile exchange of alkoxo groups - both intra-molecular, as in the case of aluminium isopropoxide[40], as well as inter-molecular. The latter type of exchange has, in fact, been utilised extensively in our as well as other laboratories for the synthesis of a wide variety of higher alkoxides and other interesting derivatives by treating lower alkoxides of different elements with higher alcohols and other hydroxy ligands like silanols[41], glycols[42], β-diketones[43-44], β-ketoesters[45], alkanolamines[46], oximes, hydroxylamines[47] and Schiff bases[48] as well as with other reagents like organic esters[49], silyl esters[50], β-ketoamines,

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thiols, thio-β-diketones[44,51], acyl halides[52], acid amides[53] and carboxylic acids as well as their anhydrides[54]. The reactions of the new alkoxides of later '3d' metals have also been investigated with a number of hydroxy agents (alkanolamines, β-diketones and carboxylic acids).

Further, sharp variations have been noticed for the first time in the alcoholysis tendencies of Cr(III)[7], Co(II)[16] and Ni(II)[18] alkoxides and these have been correlated with their varying stereochemical geometries depicting differences in thermodynamic stabilities depending on the nature of the alkyl or aryl group involved.

Alkoxides of chromium :

Methoxide and ethoxide of the most common oxidation state(III) of chromium were obtained by a novel method involving ultraviolet irradiation of tricarbonylarenechromium[55]. Primary alkoxides of chromium(III) have been synthesised recently in our laboratories by the simple reactions of $CrCl_3$.3THF adduct (which is soluble in organic solvents) with lithium alkoxides :



$$CrCl_3.3THF + 3LiOR \xrightarrow[C_6H_6]{ROH} Cr(OR)_3 + 3LiCl$$

(where R = Me, Et or Bu^n)

$Cr(OPr^i)_3$ and $Cr(OBu^t)_3$ could not be prepared by this method; some hydrolysed products were obtained instead.

All the primary alkoxides of chromium are pale green polymeric solids insoluble in organic solvents. They do not undergo alcoholysis or transesterification reactions even under forcing conditions and hence $Cr(OPr^i)_3$ or $Cr(OBu^t)_3$ could not be synthesised even through these routes. Chromium(III) phenoxide could, however, be obtained by refluxing $Cr(OEt)_3$ with excess phenol in benzene, removing the ethanol produced azeotropically with the solvent. This $Cr(OPh)_3$ was found to undergo reaction with excess isopropanol (but not with tertiary butanol) and on repeating the treatment a number of times, almost pure $Cr(OPr^i)_3$ could be obtained as a green insoluble solid. It may be of some interest that we were finally successful in synthesising $Cr(OBu^t)_3$ by an alternative simpler route, i.e., the reaction of $CrCl_3$.3THF with three moles of $LiOBu^t$ (in the absence of excess Bu^tOH) in THF itself :



$$CrCl_3.3THF + 3LiOBu^t \xrightarrow{THF} Cr(OBu^t)_3 + 3LiCl$$

$Cr(OBu^t)_3$, obtained as a soluble blue product in the above reaction, gave volatile $Cr(OBu^t)_4$, which could be distilled as a blue liquid under reduced pressure. The spectrum of this liquid shows bands at 15,700 cm^{-1}, 13,870 cm^{-1} and a shoulder at 25,300 cm^{-1}, which can be understood on the basis of a tetrahedral environment for chromium in this compound[56]. The special stability of the oxidation state(IV) for chromium in $Cr(OBu^t)_4$ also appears to be due to two singly occupied lower e_g shells.

Electronic spectra of chromium(III) alkoxides have been measured in the visible range in nujol mulls. The spectra are very similar and may be interpreted (Table 1) on the basis of an octahedral environment[56] for chromium(III).

TABLE 1—ELECTRONIC VISIBLE SPECTRA OF CHROMIUM(III) ALKOXIDES

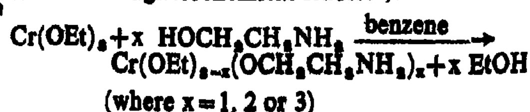
Product	$^4A_{2g} \rightarrow {}^4T_{2g}$(10Dq)	$^4A_{2g} \rightarrow {}^4T_{1g}$	B
$Cr(OMe)_3^a$	17,610 cm^{-1}	24,150 cm^{-1}	612 cm^{-1}
$Cr(OEt)_3^a$	17,000 cm^{-1}	23,470 cm^{-1}	600 cm^{-1}
$Cr(OBu^n)_3^a$	17,060 cm^{-1}	23,700 cm^{-1}	610 cm^{-1}
$Cr(OPh)_3$	16,900 cm^{-1}	23,920 cm^{-1}	615 cm^{-1}
$Cr(OMe)_3$	17,240 cm^{-1}	23,800 cm^{-1}	609 cm^{-1}
$Cr(OEt)_3^b$	16,370 cm^{-1}	23,470 cm^{-1}	654 cm^{-1}
$Cr(OPr^i)_3^b$	15,880 cm^{-1}	22,940 cm^{-1}	720 cm^{-1}
$Cr(OMe)_3^c$	17,180 cm^{-1}	24,150 cm^{-1}	613 cm^{-1}
$Cr(OPr^i)_3^c$	16,180 cm^{-1}	23,280 cm^{-1}	728 cm^{-1}

(a) Prepared from LiOR method , (b) Prepared from $Cr(OPh)_3$, (c) Prepared from $Cr(OBu^t)_4$.

The special inertness of Cr(III) alkoxides in alcoholysis reactions can be understood in the light of the stability of octahedral chromium(III), in which each of the three low energy t_{2g} orbitals are occupied singly; the John-Teller effect does not appear to be effectively operative in disturbing the regularity of this octahedral species. Cr(III) derivatives in octahedral environment, therefore, do not tend to undergo substitution reactions both by the dissociation (S_N^1) as well as associative (S_N^2) mechanisms.

Although Cr(III) primary alkoxides do not undergo alcoholysis reactions, $Cr(OPr^i)_3$ could be converted into $Cr(OMe)_3$ or $Cr(OEt)_3$ by refluxing with excess MeOH or EtOH. $Cr(OPr^i)_3$ does not, however, undergo alcoholysis reactions with tertiary or other secondary alcohols even under forcing conditions. On treatment with MeOH, EtOH or Pr^iOH, $Cr(OBu^t)_4$ readily gave the corresponding Cr(III) alkoxides, which is easily understood on the basis of greater stability of the octahedral species.

In view of the general inertness of primary alkoxides of chromium(III), a more detailed study of their substitution reactions was carried out. Although inert to other alcohols, they undergo interchange with chelating ligands like ethanolamine, β-diketones and carboxylic acids. A very wide variety of derivatives synthesised in such reactions have been characterised by their detailed spectral and magnetochemical studies[7]:



$$Cr(OEt)_3 + x\ HOCH_2CH_2NH_2 \xrightarrow{benzene} Cr(OEt)_{3-x}(OCH_2CH_2NH_2)_x + x\ EtOH$$

(where x = 1, 2 or 3)

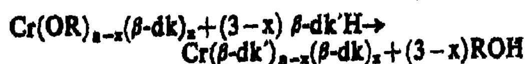
[N.B. The above reactions are slow and yield products which are insoluble in organic solvents.]



$$Cr(OR)_3 + x\ \beta\text{-dkH} \xrightarrow{\text{benzene}} Cr(OR)_{3-x}(\beta\text{-dk})_x + x\ ROH$$

[where R = Me or Et ; β-dkH = acetylacetone (acacH), benzoylacetone (bzacH) or 2-theonyltrifluoroacetone (ttaH) ; and x = 1, 2 or 3]

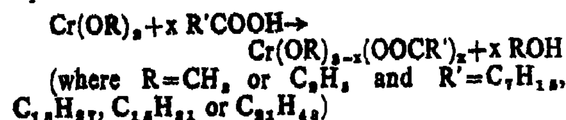
[N.B. These reactions with β-diketones are slow in the first stage, but become more facile with the formation of soluble derivatives. Products $Cr(OR)_2(\beta\text{-dk})$ are polymeric and $Cr(OR)(\beta\text{-dk})_2$ are dimeric with chromium atoms in octahedral environment.]



$$Cr(OR)_{3-x}(\beta\text{-dk})_x + (3-x)\ \beta\text{-dk}'H \rightarrow Cr(\beta\text{-dk}')_{3-x}(\beta\text{-dk})_x + (3-x)ROH$$

[N.B. In spite of their solubility, these mixed ethoxide β-diketonates also do not undergo alcoholysis with higher alcohols, but react readily with other chelating β-diketone ligands.]

Reactions of chromium alkoxides with carboxylic acids can be represented by the following equation :



$$Cr(OR)_3 + x\ R'COOH \rightarrow Cr(OR)_{3-x}(OOCR')_x + x\ ROH$$

(where R = CH_3 or C_2H_5 and R' = C_7H_{15}, $C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{21}H_{43}$)

[N.B. Reactions and products are similar to those with β-diketones ; carboxylate moieties behave as bidentate ligands. Products can be recrystallized from benzene.]

Highly oxygen sensitive (pyrophoric) alkoxides of chromium(II) have been recently reported[10] by alcoholysis of $Cr[N(SiMe_3)_2]_2.2LL'$, where L, L' = ether, THF or py. All the normal Cr(II) alkoxides (ethoxide to pentyloxide) are yellow/orange except the methoxide which is purple ; all secondary alkoxides are purple/violet and all the tertiary alkoxides are blue derivatives. Solubility of these alkoxides is influenced strongly by drying conditions. Sterically hindered alkoxides, e.g., chromium(II)-2,6-di-tertiary-butylphenoxide,

$Cr(O\text{-}C_6H_3\text{-}2,6\text{-}Bu^t_2)_2.(THF)_2$, are less associated, depict higher solubility in general and tend to form crystalline adducts with donor ligands.

Alkoxides of cobalt(II), nickel(II) and copper(II) :

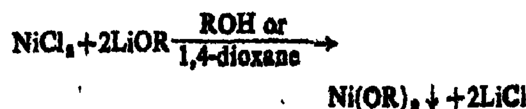
Alkoxides of these metals have been prepared[16,18] by the following reactions :



$$CoCl_2 + 2LiOR \xrightarrow[C_6H_6]{ROH} \underset{(purple)}{Co(OR)_2} \downarrow + 2LiCl$$

(where R = Me, Et or Pr^i)

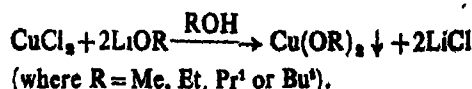
[N.B. $Co(OBu^t)_2$ could not be prepared by this method.]



$$NiCl_2 + 2LiOR \xrightarrow[1,4\text{-dioxane}]{ROH\ or} Ni(OR)_2 \downarrow + 2LiCl$$

(where R = Me, Et, Pr^n, Bu^n, Hx^n, Pr^i, Bu^s, Bu^t, Am^t or Hex^t)

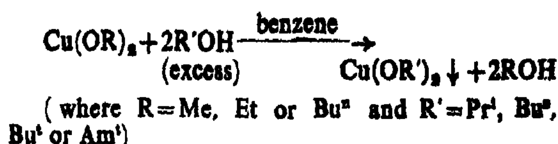
[N.B. Adducts $NiCl_2.ROH$ formed by adding $NiCl_2$ to ROH are soluble in case of primary alcohols, but insoluble in secondary or tertiary alcohols. The reactions with LiOR in the latter two cases are facilitated by addition of a little pyridine due to its solubilising effect.]



$$CuCl_2 + 2LiOR \xrightarrow{ROH} Cu(OR)_2 \downarrow + 2LiCl$$

(where R = Me, Et, Pr^i or Bu^t).

Out of the alkoxides of the above three metals, only Cu(II) alkoxides undergo facile alcohol interchange reactions similar to alkoxides of earlier transition metals :



$$Cu(OR)_2 + \underset{(excess)}{2R'OH} \xrightarrow{\text{benzene}} Cu(OR')_2 \downarrow + 2ROH$$

(where R = Me, Et or Bu^n and R' = Pr^i, Bu^s, Bu^t or Am^t)

Primary alkoxides of Co(II) and Ni(II), on the other hand, resemble those of Cr(III) in not undergoing interchange even under forcing conditions. Branched alkoxides of these metals, however, undergo facile interchange with primary alcohols even at room temperature. Extensive work has been carried out in our laboratories[18] since 1977 on the exchange reactions of nickel alkoxides with alkanolamines, β-diketones and carboxylic acids, with results similar to those described above for chromium(III) alkoxides.

Visible spectra of all the above alkoxides have been recorded in Nujol mulls and throw light on their stereochemistry. Co(II) alkoxides (purple in colour) show a multiple band in the range 18235 ± 285 cm^{-1} and a shoulder on the higher frequency side in the range 20170 ± 450 cm^{-1}. These can be explained on the basis of the ν_3 transition, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ which is characteristic for octahedral geometry of Co(II) ; these spectra are similar to those reported[17] for $Co(OMe)_2$.

Spectra of Ni(II) primary alkoxides (light green in colour) are characteristic of octahedral derivatives, which exhibit three well defined spin-allowed bands at 8750 ± 250 cm^{-1} [ν_1 ; $^3A_{2g} \rightarrow {}^3T_{2g}$] ; 14810 ± 115 cm^{-1} [ν_2 ; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$] and 24980 ± 125 cm^{-1} [ν_3 ; $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)]. The spectra of secondary and tertiary alkoxides (blue in colour) of Ni(II) clearly indicate a tetrahedral geometry with well defined spin-allowed transitions at 7580 ± 100 cm^{-1} [ν_2 ; $^3T_1 \rightarrow {}^3A_2$] and 15850 ± 70 cm^{-1} [ν_3 ; $^3T_1 \rightarrow {}^3T_1$ (P)].

The magnetic moments of the primary alkoxides of nickel(II) fall in the range of 3.45 ± 0.04 B.M. and those of secondary as well as tertiary alkoxides are found in the range of 3.65 ± 0.05 B.M. at room temperature. These observations are in accord with their octahedral and tetrahedral configurations, respectively.

TABLE 2—ELECTRONIC SPECTRA*, g VALUES (esr) AND MAGNETIC MOMENTS OF PRIMARY ALKOXIDES OF NICKEL(II)

Product	$^3A_{2g} \rightarrow {}^3T_{2g}$ (10 Dq)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3)	B	β	μ_{eff} (B.M.)	g
$Ni(OMe)_2$	8500	14700	25100	900	0.86	3.49	2.22
$Ni(OEt)_2$	8770	14490	25280	897	0.86	3.43	2.13
$Ni(OPr^n)_2$	9010	14600	24245	788	0.76	—	2.24
$Ni(OBu^n)_2$	9250	14750	23855	724	0.70	3.43	2.24
$Ni(OHex^n)_2$	9250	14925	24585	784	0.75	—	2.14
$Ni(OOct^n)_2$	9100	14815	24845	824	0.79	—	2.27

* Transitions and B in cm^{-1}

TABLE 3—ELECTRONIC SPECTRA*, g VALUES (esr) and MAGNETIC MOMENTS OF SECONDARY AND TERTIARY ALKOXIDES OF NICKEL(II)

Product	^1G	$^3T_1 \rightarrow {}^3T_1(P)$ (ν_3)	$^3T_1 \rightarrow {}^3A_2$ (ν_2)	Dq	B	β	μ_{eff} (B.M.)	g
$Ni(OPr^i)_2$	22420 sh, 18657, 17065	15900	7550	409	870	0.84	3.65	2.22
$Ni(OBu^s)_2$	22472 sh, 18657, 17033	15790	7480	384	823	0.79	3.70	2.25
$Ni(OBu^t)_2$	22625 sh, 18618, 17007	15920	7680	395	827	0.79	3.61	2.23
$Ni(OAm^t)_2$	22522 sh, 18485, 16950	15850	7520	390	833	0.80	3.67	2.23

* Transitions, Dq and B in cm^{-1}.

TABLE 4—ELECTRONIC SPECTRA OF A FEW OTHER TYPICAL NICKEL(II) DERIVATIVES

Derivative	$^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1, 10 Dq)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3)	B	β
$NiCl_2$ MeOH	7937	13833	22400	795	0.74
$NiCl_2$ Pr^iOH	7924	12908	21978	740	0.68
$NiCl_2.Am^tOH$	7520	12195	21740	758	0.70
$Ni(OMe)Cl$*	7900	12900	22100	753	0.72
$Ni(OMe)Cl$ MeOH*	8100	13300	24000	866	0.83
$Ni(OEt)Cl$*	8000	13200	23610	854	0.82
$Ni(OPr^i)Cl$*	8200	13100	22500	733	0.70
$Ni(OMe)(OCH_2CH_2NH_2)$@	9090	14390	23065	680	0.63
$Ni(OPr^i)(OCH_2CH_2NH_2)$@	9090	14925	25562	881	0.82
$Ni(OCH_2CH_2NH_2)$@	9015	14925	23516	640	0.59
$Ni(OMe)(acac)$°	8930	15528	24904	909	0.84
$Ni(OPr^i)(acac)$°°	8970	14706	23098	726	0.67
$Ni(OBu^t)(acac)$°°	9260	14860	24155	749	0.69
$Ni(acac)_2$°°	8800	15267	25210	938	0.87
$Ni(OMe)(OOC.C_{13}H_{27})$†	8585	14620	24272	876	0.84
$Ni(OPr^i)(OOC.C_{13}H_{27})$†	8695	14663	24155	849	0.81
$Ni(OBu^t)(OOC.C_{13}H_{27})$†	8695	14577	23923	828	0.79
$Ni(OOC.C_{13}H_{27})_2$†	8930	15015	23520	784	0.75

* Soluble in parent alcohols and undergo alcoholysis reactions

@ Insoluble in organic solvents and do not undergo alcoholysis reactions

° Soluble in organic solvents in which it shows tetrameric association

°° Soluble in organic solvents in which they show trimeric association

† Soluble in organic solvents, primary alkoxy derivatives do not undergo alcoholysis but secondary and tertiary alkoxy derivatives undergo alcoholysis

The ligand field, (Dq), and Racah, (B), parameters for the tetrahedral secondary and tertiary alkoxides of nickel (Table 3) were calculated by the method of Underhill and Billing[28]. As expected, the magnitude of 10 Dq values obtained in all the tetrahedral complexes are about four-ninth of the 10 Dq values observed (Table 2) for the corresponding octahedral compounds. The values of B in both octahedral and tetrahedral derivatives are found to be reduced below the free ion value (1041 cm^{-1}) showing an appreciable covalent character of the metal-ligand bonds in these alkoxide derivatives.

At room temperature, all octahedral as well as tetrahedral nickel(II) alkoxides give one signal in their electron spin resonance spectra in the polycrystalline state from which Lande splitting factors (g values) have been calculated to lie in the range 2.13-2.27 (Tables 2 and 3), indicating again a strong covalent character of the metal-ligand bonds in these complexes.

It may be interesting to record that the electronic spectra (Table 4) of a large number of allied derivatives of nickel(II), prepared by reactions represented for the sake of brevity by the

following equations, indicate an octahedral environment for nickel in all these cases (including those with ramified alkoxy ligand) :



$$NiCl_2 + x\,ROH \xrightarrow{\text{reflux}} NiCl_2.x\,ROH$$



$$\downarrow \text{heat}$$



$$NiCl_2.ROH$$

(where R = CH_3, C_2H_5, $C_3H_7{}^n$, $C_4H_9{}^n$, $C_5H_{11}{}^n$ or $C_8H_{17}{}^n$ and x = 1 – 4 at room temperature.)



$$NiCl_2.MeOH + R'OH \longrightarrow NiCl_2.R'OH + MeOH\uparrow$$

(where R' = $C_3H_7{}^i$, $C_4H_9{}^t$ or $C_5H_{11}{}^t$; $NiCl_2$ does not dissolve or react with secondary and tertiary alcohols and the adducts could be prepared in these cases by alcohol interchange reactions only.)



$$NiCl_2 + NaOR \xrightarrow{ROH} Ni(OR)Cl + NaCl\downarrow$$

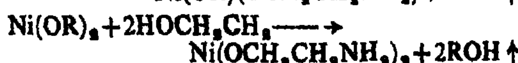


$$Ni(OR)Cl + R'OH \xrightarrow{C_6H_6} Ni(OR')Cl + ROH\uparrow$$

(where R and R' = CH_3, C_2H_5, $C_3H_7{}^i$, $C_4H_9{}^n$ or $C_8H_{17}{}^n$)

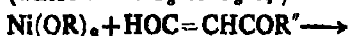


$$Ni(OR)_2 + HOCH_2CH_2NH_2 \longrightarrow Ni(OR)(OCH_2CH_2NH_2) + ROH\uparrow$$

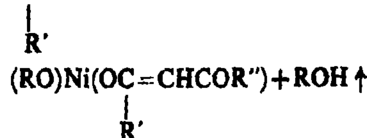


$$Ni(OR)_2 + 2HOCH_2CH_2 \longrightarrow Ni(OCH_2CH_2NH_2)_2 + 2ROH\uparrow$$

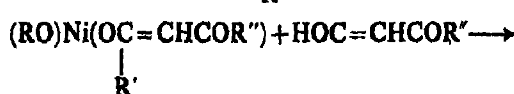
(where R = CH_3 or $C_3H_7{}^i$)



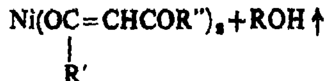
$$Ni(OR)_2 + HOC(R'){=}CHCOR'' \longrightarrow$$



$$(RO)Ni(OC(R'){=}CHCOR'') + ROH\uparrow$$



$$(RO)Ni(OC(R'){=}CHCOR'') + HOC(R'){=}CHCOR'' \longrightarrow$$



$$Ni(OC(R'){=}CHCOR'')_2 + ROH\uparrow$$

(where R = CH_3 or $C_3H_7{}^i$;
R' = R'' = CH_3, C_6H_5, CF_3 or C_4H_3S)



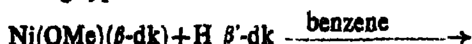
$$Ni(OR)_2 + R'COOH \rightarrow Ni(OR)(OOCR') + ROH\uparrow$$



$$Ni(OR)_2 + 2R'COOH \rightarrow Ni(OOCR')_2 + 2ROH\uparrow$$

(where R = CH_3 or $C_3H_7{}^i$, R' = $C_{13}H_{27}$, $C_{15}H_{31}$ or $C_{17}H_{35}$).

A few mixed β-diketonates and carboxylates of nickel(II) could also be synthesised by the following types of reactions :



$$Ni(OMe)(\beta\text{-dk}) + H\ \beta'\text{-dk} \xrightarrow{\text{benzene}}$$



$$Ni(\beta\text{-dk})(\beta'\text{-dk}) + MeOH\uparrow$$

$$Ni(OOC.CH_3)_2 + RCOOH \xrightarrow{\text{toluene}} Ni(OOC.CH_3)(OOC.R) + CH_3COOH\uparrow$$

Nickel alkoxides undergo insertion reactions[59] also with substrates like isocyanates and these reactions can be represented as :



$$Ni(OR)_2 + n\,R'NCO \rightarrow (RO)_{2-n}Ni[N(R')COOR]_n$$

(where R = Me or Pr^i ; R' = Ph or naph ; n = 1 or 2).

All these reactions are exothermic in benzene and their completion was indicated by the disappearance of the band at ~2250 cm^{-1} (due to –N=C=O).

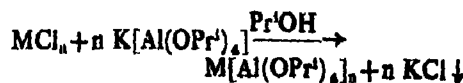
The appearance of an intense band at 1700 cm^{-1} (due to C=O) in the addition products suggests that the insertion has occurred at the C=N site.

The spectra of the branched green alkoxides of copper, viz., $Cu(OPr^i)_2$, $Cu(OBu^s)_2$, $Cu(OBu^t)_2$ and $Cu(OAm^t)_2$ are characterised by broad absorptions in the visible range around 15200 ± 635 cm^{-1} which generally tail deep into the near infrared region. This band can be assigned as a $^2E_g \rightarrow {}^2T_{2g}$ transition, which is characteristic of Cu^{2+} in six coordinate tetragonal geometry. In addition to a sharper absorption in this region at 15500 ± 70 cm^{-1}, another band appears around 19100 ± 300 cm^{-1} in the spectra of blue primary alkoxides, $Cu(OMe)_2$, $Cu(OEt)_2$ and $Cu(OBu^n)_2$ which indicates a distorted octahedral environment around copper(II) in these derivatives.

Magnetic susceptibilities of copper alkoxides show a lowering in the value with decrease in temperature [$Cu(OAm^t)_2$: 1.83 at 297° to 1.37 at 87°K ; $Cu(OPr^i)_2$: 1.50 at 297° to 0.98 at 88°K and $Cu(OBu^n)_2$: 1.18 at 299° to 0.64 at 88°K], which suggests antiferromagnetic exchange interaction between copper pairs in all these alkoxides, based on infinite chains[60] of methoxy bridged copper atoms rather than a layer type structure suggested earlier[61]. The values of exchange coupling constants (j) in these alkoxides have been calculated on the basis of Ising theory[62] as 129, 81 and 43 cm^{-1} respectively for $Cu(OBu^n)_2$, $Cu(OPr^i)_2$ and $Cu(OAm^t)_2$.

Bimetallic alkoxides of chromium(III), manganese(II), iron(II and III), cobalt(II), nickel(II) and copper(II) with aluminium :

Bimetallic isopropoxides of the above elements with aluminium have been prepared by the following reactions :



$$MCl_n + n\,K[Al(OPr^i)_4] \xrightarrow{Pr^iOH} M[Al(OPr^i)_4]_n + n\,KCl\downarrow$$

[where n = 3 for Fe(III) and n = 2 for Mn(II), Fe(II), Co(II), Ni(II) or Cu(II)].

In view of the insolubility of $CrCl_3$ in organic solvents, its adduct $CrCl_3.3THF$ was used as a starting material for a similar preparation of $Cr[Al(OPr^i)_4]_3$. All these reactions are exothermic. The products are coloured liquids/solids which are miscible/soluble in organic solvents and can be purified by distillation under reduced pressure. All of these depict monomeric behaviour in refluxing benzene.

These bimetallic isopropoxides react quantitatively with excess of ethanol, 2,2,2-trifluoroethanol and normal butanol to give the corresponding

derivatives which are also volatile and soluble in organic solvents :



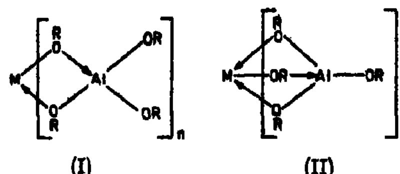
$$M[Al(OPr^i)_4]_n + 4n\ ROH \xrightarrow{\text{benzene}} M[Al(OR)_4]_n + 4n\ Pr^iOH \uparrow$$

The products, $M[Al(OMe)_4]_n$, obtained with excess methanol, however, are insoluble and non-volatile. The reactions with methanol were carried out in the case of $Cr[Al(OPr^i)_4]_3$ in 3 : 1 and 6 : 1 molar ratios also, yielding respectively $Cr[Al(OPr^i)_3(OMe)]_3$ and $Cr[Al(OPr^i)_2(OMe)_2]_3$; the former is soluble whereas the latter is only sparingly soluble in benzene.

Exchange reactions with excess tertiary alcohols, however, yielded interesting end products of the following types, $M[Al(OPr^i)(OBu^t)_3]_2$, $M[Al(OPr^i)_2(OAm^t)_2]_2$, $M[Al(OPr^i)_2(OBu^t)_2]_3$ and $M[Al(OPr^i)_2(OAm^t)_2]_3$. All these bimetallic derivatives could also be purified, unchanged, by distillation under reduced pressure and showed monomeric behaviour in refluxing benzene.

Isopropoxide acetylacetonate products, $M[Al(OPr^i)_{4-x}(acac)_x]_{2\ or\ 3}$ (where x = 1 or 2), obtained by treating the bimetallic isopropoxides with stoichiometric quantities of acetylacetone have again been shown to be volatile monomeric products. Products of the types, $M[Al(OPr^i)_{4-x}(acac)_x]_{2\ or\ 3}$ (where x = 3 or 4) tended to dissociate into metal isopropoxide or acetylacetonate and aluminium acetylacetonate.

The chemical reactions as well as spectroscopic and magnetic properties of the above interesting derivatives appear to indicate that most of these derivatives have structure (I) similar to those suggested earlier[83], but the data for a few cobalt, nickel and copper derivatives appear to be more easily understood on the basis of a structure of the type (II).



(I) (II)

A similar conclusion has been reported by Stumpp and Hillebrand[87] for products, $M[Al(OR)_4]_2$ ($M = Co$, Ni or Cu ; $R = CH_3$, C_2H_5, $C_3H_7^n$ or $C_4H_9^n$) in a later publication.

The above tendency to attain octahedral geometry, for example, by $Ni[Al(OR)_4]_2$ derivatives, appears to increase as the alkoxy groups become smaller and less ramified. According to detailed

TABLE 5—BIMETALLIC ALKOXIDES AND ALLIED DERIVATIVES OF LATER '3d' TRANSITION METALS

Compound	Nature	Volatility (°C/...mm)	M.W. Found (Calcd.)	μ_{eff} (B.M./°K)	D_q (cm^{-1})
$Cr[Al(OPr^i)_4]_3$	Green viscous liquid	190/0.6	838 (842)	3.90/100	1527
$Mn[Al(OPr^i)_4]_2$	Brown viscous liquid	145/0.6	607 (582)	5 95/88 5.90/297	—
$Fe[Al(OPr^i)_4]_3$	Brown viscous liquid	130/0.8	1008 (846)	5.06/89 5.39/296	—
$Fe[Al(OPr^i)_4]_2$	Brown semi-solid	125/0 8	605 (582)	4.58/87 5 06/297	—
$Co[Al(OPr^i)_4]_2$	Purple liquid	140/0 6	629 (586)	4.62/92 4.39/297	873
$Ni[Al(OPr^i)_4]_2$	Pink liquid	120/0.6	570 (585)	3.29/90 3.39/294	828 (film) 895 (Pr^iOH) 912 (pyridine)
$Cu[Al(OPr^i)_4]_2$	Greenish blue liquid	135/0.6	604 (593)	1.22/87 1.64/297	1880
$Cr[Al(OPr^i)_3(OMe)]_3$	Lightgreen solid	215/0.8	—	3.84/300	1572
$Cr[Al(OPr^i)_2(OMe)_2]_3$	Green solid	255/0 8*	—	3.86/300	1582
$Cr[Al(OEt)_4]_3$	Green solid	235/0.8*	—	3 88/300	1577
$Cr[Al(OCH_2CF_3)_4]_3$	Brown viscous liquid	120/0.8*	1858 (1821)	3 86/300	1520
$Cr[Al(OPr^i)_3(acac)]_3$	Green pasty solid	140/0 8	967 (962)	3 82/300	1675
$Cr[Al(OPr^i)_2(acac)_2]_3$	Green solid	180/0.8*	1288 (1082)	3.83/300	1692
$Fe[Al(OPr^i)_2(OAm^t)_2]_3$	Brown solid	270/0.6*	976 (1014)	—	—
$Ni[Al(OPr^i)(OBu^t)_3]_2$	Purple solid	140/0.6*	691 (670)	3.14/88 3.47/300	786
$Ni[Al(OPr^i)_2(acac)_2]_2$	Brown pinkish solid	240/0.6*	708 (745)	3.28/300	769
$Cu[Al(OCH_2CF_3)_4]_2$	Blue semi-solid	115/0.5	—	1.72/300	1602
$Cu[Al(OPr^i)(OBu^t)_3]_2$	Green solid	150/0.5*	—	1.74/300	1290 (benzene) 1490 (Nujol)

* Sublimed.

investigations carried out by Singh[16] in our laboratories, $Ni[Al(OMe)_4]_2$ shows an electronic spectrum fully characteristic of octahedral geometry for nickel. $Ni[Al(OEt)_4]_2$ and $Ni[Al(OPr^i)_4]_2$, on the other hand, show increasing proportions of tetrahedral nickel species in equilibrium with octahedral forms. The effects of steric factors on this type of equilibrium can be discerned in a finer difference, i.e., the spectrum of $Ni[Al(OEt)_4]_2$ in ethanol shows a complete shift to octahedral species whereas for $Ni[Al(OPr^i)_4]_2$ in isopropanol, this type of shift is only partial and a stronger donor molecule like pyridine only is able to shift the same fully to the octahedral form.

Detailed physico-chemical measurements (volatility, molecular association, electronic and esr spectra as well as magnetic moments at varying temperatures) have been carried out on all the bimetallic alkoxides and products derived from them. For brevity, only a few illustrative physical data for some typical bimetallic alkoxides of later '3d' transition metals with aluminium and their mixed derivatives are given in Table 5. Investigations are now being extended to the bimetallic systems consisting of the above transition elements with new ligands like $[Ga(OR)_4]^-$; $[Zr_2(OPr^i)_9]^-$; $[Hf_2(OPr^i)_9]^-$; $[Nb(OR)_6]^-$ and $[Ta(OR)_6]^-$.

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Studies on Reactivity of Molybdenyl(V) Cation in the Environment of Diverse Anions in Presence of 5-Nitro 1,10-Phenanthroline as an Organic Base

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New salts of oxohalomolybdate(V) ions, 5-nitro 1,10-phenanthroline oxopentachloro- and pentabromo molybdates, (5-nitrophenH$_2$) [MoOX$_5$] (X = Cl, Br), have been isolated in pure form for the first time. Reactions of these salts both in solution and in solid state lead to the synthesis of nonelectrolytic *cis*-[MoOX$_3$ 5-nitrophen], oxalato derivative [MoO OX.Cl.5-nitrophen] and hydrolytic products [Mo$_2$O$_4$X$_2$(5-nitrophen)$_2$]. These compounds have been characterised by analytical and other physico-chemical techniques.

DEFINITE involvement of quinquevalent molybdenum in various biometabolisms has undoubtedly been confirmed by several authors[1,2] for a long time. The chemistry of quinquevalent molybdenum is largely dominated by the oxomolybdenum "MoO^{3+}" species which undergoes various chemical changes in different anionic environments[3-5] at different conditions.

The present communication deals with the systematic study of the reactions of the molybdenyl cation MoO^{3+} in both halide and oxalate anionic environments in solutions and also in solid state, in presence of the ligand having [-N-C-C-N-] kind of linkage which has been demonstrated by the isolation of the salts of the type $LH_2[MoOX_5]$, nonelectrolytes $MoOX_3.L$, oxalato derivative of the nonelectrolytic [MoO(OX)Cl.L] etc. (where L = 5-nitro 1,10-phenanthroline and X = Cl, Br) for the first time. Close examination of the chemistry of pentavalent molybdenum clearly reveals that the characteristic chemical behaviour of the compounds largely depends on the basic nature of the organic ligands associated with them The authors were, therefore, interested in exploring the differential activities of these quinquevalent molybdenum compounds particularly in presence of the substituted 1,10-phenanthroline e g , 5-nitro 1,10 phenanthroline. It is interesting to note in this connection that the presence of a nitro group at the 5-position of the 1,10-phenanthroline in the ligand does not considerably affect the pronounced potentiality of the heterocyclic nitrogens. This is probably due to the fact that electron withdrawing nitro group is far apart from the basic nitrogen atoms.

The stereochemical constructions of the nonelectrolytes have been established by the present authors through the isolation and study of the hydrolytic products $[Mo_2O_4.X_2.L_2]$. Thermogravimetric investigations of the salts clearly indicate the course through which the dehydrohalogenation and other transformations have taken place in solid state.

The compounds have been characterised by elemental analysis and other physico-chemical investigations.

Experimental

All reagents used were of A.R. grade. Molybdenum and halogens[3-4] were estimated gravimetrically as MoO_3, AgCl and AgBr, respectively. Nitrogen was estimated by Dumas' method. Oxalate was estimated by the standard $KMnO_4$ method applied to other similar[6] oxalato complexes. Oxidation state of the metal was determined by ceric sulphate method.

Preparation

1. *5-Nitro 1,10-phenanthrolinium oxopentachloromolybdate(V), 5-nitrophenH$_2$[MoOCl$_5$] :* About 1.0 g of molybdenum trioxide was dissolved in 10 ml hot conc. hydrochloric acid with stirring followed by addition of 1 ml hydroiodic acid. The solution was boiled to drive off the liberated iodine. The concentrated small mass was taken up with minimum quantity of conc. hydrochloric acid when a bright green solution was obtained To this solution, containing $[MoOCl_5]^{2-}$, was added with stirring a solution of 1.56 g of 5-nitro 1,10 phenanthroline in minimum quantity of conc. hydrochloric acid. The mixture was cooled in ice when a yellowish green precipitate was obtained. The product was filtered and dried to constant weight in vacuum desiccator over solid KOH. Yield, about ?.5 g. Found : Mo, 18.92 ; Cl, 33.90 ; N, 7.8. Calcd. for $C_{12}H_9N_3O_3MoOCl_5$ i.e., 5-nitrophenH$_2$-[MoOCl$_5$] ; Mo, 18.57 ; Cl, 34.42 ; N, 8.1%. Oxidation state of the metal was found to be 5.16.

2. *Oxotrichloro (5-nitro 1,10 phenanthroline) molybdenum(V), [$MoOCl_3$. 5-nitrophen]* : 1.0 g of the salt 5-nitrophenH_2[$MoOCl_5$] was refluxed with 10 ml of dehydrated ethanol for 1 hr. The mixture was cooled when a shinning chocolate colour crystalline product precipitated. This was filtered, washed with minimum quantity of dehydrated ethanol and dried in vacuum desiccator over solid KOH to constant weight. Yield, about 0.72 g. Found : Mo, 21.72 ; Cl, 23.57 ; N, 9.1. Calcd. for $C_{12}H_7N_3O_2MoOCl_3$ i.e., [$MoOCl_3$.5-nitrophen] ; Mo, 21.64 ; Cl, 24.01 ; N, 9.47%. Oxidation state of the metal was found to be 5.12.

This compound can also be prepared by dehydrohalogenation of the salt 5-nitrophenH_2[$MoOCl_5$] by heating at 130° in a tube furnace in a current of dry CO_2.

3. *Oxo-μ-dioxochloro(5-nitro 1,10-phenanthroline)-molybdenum(V), [$Mo_2O_4Cl_2$(5-nitrophen)$_2$]* : About 1.0 g of 5-nitrophenH_2[$MoOCl_5$] was gently boiled with 10 ml of 1 : 2 ethanol-water mixture for 15 min. The orange solid compound so precipitated was filtered and washed twice with cold water. It was dried in vacuum desiccator over solid KOH. Yield, about 0.7 g. Found : Mo, 24.58 ; Cl, 9.63 ; N, 10.55. Calcd. for [$Mo_2O_4Cl_2$(5-nitrophen)$_2$] ; Mo, 24.7 ; Cl, 9.13 ; N, 10.81%. Oxidation state of the metal was found to be 4.86.

This compound can also be prepared from the non-electrolyte [$MoOCl_3$.5-nitrophen] by hydrolysis. This reaction suggests the probable *cis*-configuration of [$MoOCl_3$.5-nitrophen] as hydrolysis is followed by *trans*-elimination reaction.

4. *Oxochloro oxalato(5-nitro 1,10-phenanthroline)-molybdenum(V), [MoO(OX)Cl.5-nitrophen]* : About 0.562 g of freshly prepared [$MoOCl_3$.5-nitrophen] was mixed with powdered oxalic acid in the 1 : 1 mole ratio and the resulting mixture was heated at an optimum temperature of 130° in a tube furnace in an atmosphere of dry CO_2 till the evolution of hydrogen chloride ceased. The grey coloured product was washed with minimum quantity of dehydrated ethanol until free from unreacted oxalic acid and dried in vacuum desiccator over solid KOH. Yield, about 0.4 g. Found : Mo, 20.82 ; Cl, 7.73 ; $C_2O_4^{2-}$, 19.74 ; N, 9.1. Calcd. for [MoO(OX). Cl.5-nitrophen] ; Mo, 20.84 ; Cl, 7.70 ; $C_2O_4^{2-}$, 19.1 ; N, 9.12%. Oxidation state of the metal was found to be 4.96.

An attempt was made to hydrolyse this oxalato derivative but no pure compound could be isolated.

5. *5-Nitro 1,10-phenanthrolinium oxopentabromomolybdate(V), 5-nitrophenH_2[$MoOBr_5$]* : About 1.0 g of molybdenum trioxide was gently reduced with 10 ml 48% boiling hydrobromic acid and was evaporated almost to dryness. The residual mass was taken up with 10 ml 48% hydrobromic acid and the operation repeated twice. Finally, the residue was dissolved in 10 ml of the same boiling acid and 1.56 g of 5-nitro 1,10-phenanthroline, dissolved in minimum quantity of the same acid was added to this with stirring. The mixture on cooling to room temperature yielded a yellow crystalline solid compound. The product was filtered, washed with hydrobromic acid and dried in vacuum desiccator over solid KOH to constant weight. Yield, about 4.6 g. Found : Mo, 12.98 ; Br, 54.16 ; N, 5.5. Calcd. for $C_{12}H_9N_3O_2MoOBr_5$ i.e., 5-nitrophenH_2[$MoOBr_5$] ; Mo, 12.99 ; Br, 54.12 ; N, 5.68%. Oxidation state of the metal was found to be 4.88.

6. *Oxotribromo(5-nitro 1,10-phenanthroline)-molybdenum(V), [$MoOBr_3$.5-nitrophen]* : About 1.0 g of 5-nitrophenH_2[$MoOBr_5$] was heated in a tube furnace at 150° in an atmosphere of dry CO_2 till the evolution of hydrogen bromide ceased. The orange red product was washed with minimum quantity of dehydrated ethanol and dried in vacuum desiccator over solid KOH to constant weight. Yield, about 0.5 g. Found : Mo, 16.22 ; Br, 42.48 ; N, 7.05. Calcd. for $C_{12}H_7N_3O_2MoOBr_3$ i.e., [$MoOBr_3$.5-nitrophen] ; Mo, 16.63 ; Br, 41.59 ; N, 7.27%. Oxidation state of the metal was found to be 5.11.

The attempted dehydrohalogenation of the salt 5-nitrophenH_2[$MoOBr_5$] in dehydrated ethanolic solution failed due to the formation of impure products.

7. *Oxo-μ-dioxobromo(5-nitro 1,10-phenanthroline)-molybdenum(V), [$Mo_2O_4Br_2$.(5-nitrophen)$_2$]* : About 1.2 g of 5-nitrophenH_2 [$MoOBr_5$] was treated with 10 ml of 1 : 2 ethanol water mixture and boiled for 15 min. A brown solid precipitated on cooling to room temperature. The product was washed twice with cold water and dried in vacuum desiccator over solid KOH to constant weight. Yield, about 0.5 g. Found : Mo, 21.49 ; Br, 19.10 ; N, 9.50%. Calcd. for [$Mo_2O_4Br_2$.(5-nitrophen)$_2$] ; Mo, 22.17 ; Br, 18.45 ; N, 9.69%.

This compound can also be prepared by the hydrolysis of the non-electrolyte [$MoOBr_3$.5-nitrophen] by ethanol-water mixture. By this reaction the *cis*-configuration of the non-electrolyte has been established as hydrolysis proceeds through *trans*-elimination reaction.

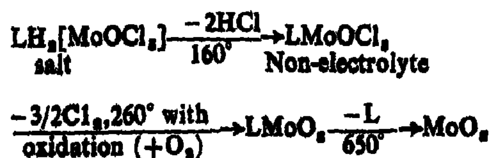
Conductance measurements : Molar conductances at different dilutions were measured in aqueous medium in a "dip type" cell for the salts 5-nitrophenH_2[$MoOX_5$] (X = Cl, Br). The results showed that the salts were extensively hydrolysed in aqueous solution. Conductances of [$MoOX_3$.5-nitrophen] and [MoO(OX)Cl.5-nitrophen] were measured in nitrobenzene solution. These are 3.01, 1.63 and 3.63 ohm^{-1} cm^2 $mole^{-1}$ for chloro, bromo and oxalato derivatives, respectively. These values are much less than those for binary electrolytes[7] indicating non-electrolytic nature of the compounds in conformity with their molecular formula. No suitable solvents, however, could be found for [$Mo_2O_4X_2$.(5-nitrophen)$_2$].

Magnetic susceptibility measurements : Magnetic susceptibilities of the compounds were measured

in Gouy balance using a field strength of 8500 gauss. The values of the μ_{eff} are 1.67(300), 1.43(300), 0.706(295), 1.88(300), 1.72(300), 1.71(303) and 0.69(297) B.M. for 5-nitrophen$H_2[MoOCl_5]$, $[MoOCl_3.5\text{-nitrophen}]$, $[Mo_2O_4Cl_2.(5\text{-nitrophen})_2]$, $[MoO(OX)Cl.5\text{-nitrophen}]$, 5-nitrophen$H_2[MoOBr_5]$, $[MoOBr_3.5\text{-nitrophen}]$ and $[Mo_2O_4Br_2(5\text{-nitrophen})_2]$, respectively. (Figures in the parentheses are the temperatures in the absolute scale). Values of μ_{eff} are calculated as $\mu_{eff}=2.839\ (X'_M.T)^{\frac{1}{2}}$ B.M., where X'_M=corrected molar susceptibility X_M+X_d (X_M being the uncorrected value and χ_d the diamagnetic correction for ligands). The values are in fair agreement with the d^1 configuration of the quinquevalent molybdenum. The hydrolytic product $[Mo_2O_4X_2.(5\text{-nitrophen})_2]$ has small values of magnetic moment due to oxobridges[8] with the possible Mo–Mo interaction.

Thermogravimetric analysis : Thermogravimetric investigations were carried out in MOM derivatograph, Hungary, for recording DTA, the rate of heating being 10°/min. The thermo-couple was Pt-Pt-Rh. The reference inert sample was $\alpha-Al_2O_3$. The results of the thermogravimetric analysis of the salts $LH_2[MoOX_5]$ (X=Cl, Br and L=5-nitrophen) are plotted in Figs. 1 and 2 Investigations were made under the influence of dynamic dry air. It is evident from the curves that the chloro salt $LH_2[MoOCl_5]$ undergoes loss of weight near 130° and becomes stable to the nonelectrolytic form $[LMoOCl_3]$ with the elimination of two molecules of hydrogen chloride at 160° as supported by the strong endothermic peak of the DTA curve. Dehydrohalogenation takes place with 13.6% loss of weight against the theoretically estimated value of 14.1%. The slight deviation may be due to the presence of moisture in the sample.

The second medium sharp endothermic change occurs at 260° indicating the formation of the stable oxidised form $LMoO_2$ with the observed 30.9% weight loss against the anticipated value of 29.0%. The discrepancy between these values suggests that the decomposition is incomplete at this temperature and an intermediate compound must be formed. Finally, the formation of the most stable final product MoO_2 with the elimination of one molecule of ligand per molecule of $LMoO_2$ has been indicated with the 72.9% loss of weight in comparison to the theoretical loss of 72.1%. The compound starts loss of weight around 550° and becomes stable at 650° as a weak and sharp endothermic peak appears at 650°. This is also supported by the DTA curve. The successive changes may be represented schematically as follows :



$$\underset{\text{salt}}{LH_2[MoOCl_5]}\xrightarrow[160^\circ]{-2HCl}\underset{\text{Non-electrolyte}}{LMoOCl_3}$$

$$\xrightarrow[\text{oxidation }(+O_2)]{-3/2Cl_2,260^\circ\text{ with}}LMoO_2\xrightarrow[650^\circ]{-L}MoO_2$$

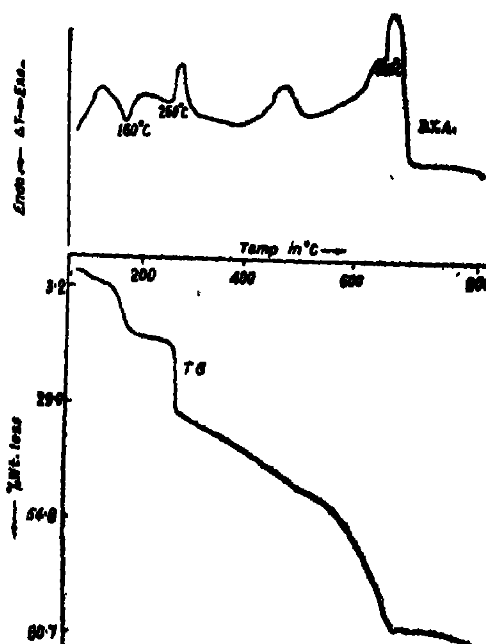


Fig. 1. T. G. and D. T. A. curves for 5-nitrophen $H_2[MoOCl_5]$

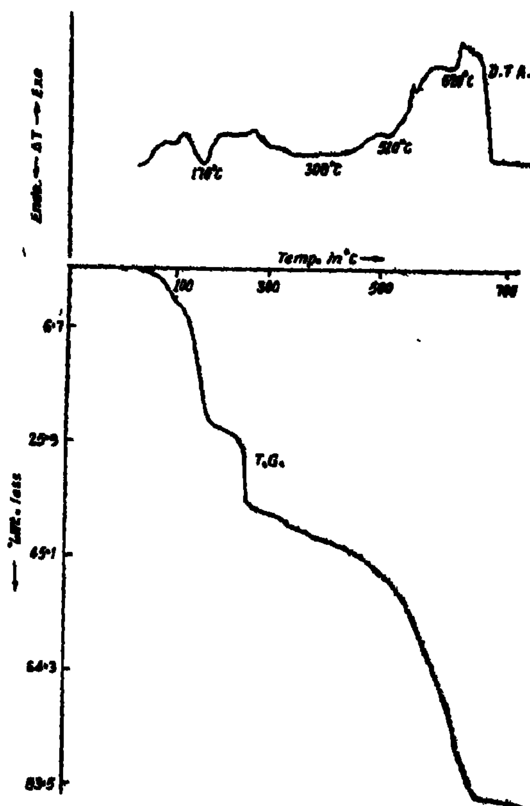
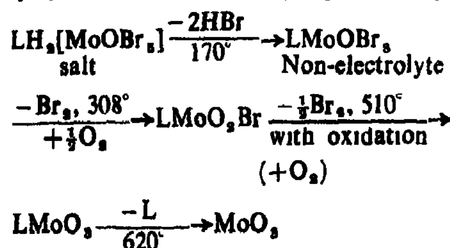


Fig. 2. T. G. and D. T. A. curves for 5-nitrophen $H_2[MoOBr_5]$.

In contrast to the chloro salt, the bromo sa[lt] $LH_2[MoOBr_5]$ starts loss of weight near 100° an[d] becomes stable to the nonelectrolytic for[m]

$LMoOBr_3$, with the elimination of two molecules of hydrogen bromide per molecule of the compound at 170°, as is evident from the strong and sharp endothermic peak in the DTA curve. The dehydrohalogenation takes place with 22.9% loss of weight in comparison to the anticipated value of 22.0%. The small deviation may be due to the adhered moisture of the sample.

The second broad and medium endothermic band appears at 308° in the DTA curve indicating the formation of the intermediate $LMoO_2Br$, with the observed 40.2% loss of weight against the theoretical value of 41.4%. The third endothermic change probably occurs at 510° as is evident from the DTA curve. The formation of the oxidised form, $LMoO_3$, may be suggested with the 48% observed loss of weight against the theoretical value of 50%. Finally, the most stable state, MoO_3, is attained at 620° with the elimination of one molecule of ligand per molecule of the parent $LMoO_3$. The compound starts loss of weight at 550° and becomes constant at 620° as indicated by the TG diagram. The formation of the stable oxide has been verified as the observed loss is about 79% in comparison with the theoretical loss of 80.5%. So the process of oxidation of the bromo-salt, which proceeds via the formation of the nonelectrolyte, involves the following suggested steps :



$$\underset{\text{salt}}{LH_2[MoOBr_5]} \xrightarrow[170^\circ]{-2HBr} \underset{\text{Non-electrolyte}}{LMoOBr_3}$$

$$\xrightarrow[+\frac{1}{2}O_2]{-Br_2,\ 308^\circ} LMoO_2Br \xrightarrow[\text{with oxidation } (+O_2)]{-\frac{1}{2}Br_2,\ 510^\circ}$$

$$LMoO_3 \xrightarrow[620^\circ]{-L} MoO_3$$

Infrared spectra : IR spectra of the compounds were recorded in Perkin-Elmer IR spectrophotometer using KBr pellets. The main bands are given in Table 1. IR spectra of the compounds show strong absorption bands in the region 930-980 cm^{-1} due to the Mo(V)=O stretching vibration[3,4]. The metal-oxygen chain (-Mo-O-Mo-O) vibration may be located in the broad bands in the region 700-800 cm^{-1} in the hydrolytic products $Mo_2O_4X_2$-(5-nitrophen)$_2$. IR bands of the non-electrolytic oxalato derivative [MoO(OX)Cl.(5-nitrophen)] around 1630 cm^{-1} may be assigned to the $\nu_{C=O}$ stretching, 1330 cm^{-1} to the $\nu_{C-O}+\nu_{C-C}$ stretching and 910 cm^{-1} and 1200 cm^{-1} to the $\nu_{C-O}+\delta_{O-C=O}$ stretching. The assignments on the oxalato derivative were made on the basis of the previous[6] work on oxalato complexes.

Electronic spectra : The solution spectra of the compounds were recorded in Varian Series 634 UV spectrophotometer using AnalaR grade solvents. Hydrochloric acid, 12 *M*, was used as a solvent for 5-nitrophenH$_2$[$MoOCl_5$] and AnalaR grade acetonitrile for the non-electrolytic complex [$MoOCl_3$.5-nitrophen] including oxalato derivative. The solvent used in the case of 5-nitrophenH$_2$[$MoOBr_5$] was 48% HBr and AnalaR grade acetonitrile for the nonelectorlytic complex [$MoOBr_3$.5-nitrophen]. No suitable solvent could be found for the binuclear complexes [$Mo_2O_4Cl_2$.(5-nitrophen)$_2$] and [Mo_2O_4-Br_2.(5-nitrophen)$_2$] and their reflectance spectra were taken in solid state using paraffin base.

The assignments made on the basis of observation in identical cases[6-11] are tabulated in Tables 2 and 3.

TABLE 1—INFRARED BANDS IN cm^{-1}

Compound	Main bands
5-nitrophenH$_2$[$MoOCl_5$]	600w, 700m, 715m, 810vs, 895s, 980vs, 1330s, 1365vs, 1415w, 1450w, 1540vs, 1620sb, 1680w, 3070w, 3270wb.
[$MoOCl_3$ 5-nitrophen]	650vw, 720s, 760w, 820s, 840s, 900m, 940w, 970vs, 1150m, 1380vs, 1420s, 1520vs.
[$Mo_2O_4Cl_2$(5-nitrophen)$_2$]	710m, 800w, 825m, 940vs, 1140w, 1320s, 1420m, 1510vs.
[MoO(OX)Cl.5-nitrophen]	660w, 720s, 740w, 760m, 825s, 840s, 910mb, 940w, 970vs, 1120w, 1150m, 1200w, 1330vs, 1420s, 1680w, 1750mb.
5-NitrophenH$_2$[$MoOBr_5$]	690m, 710w, 800s, 880m, 980s, 1090w, 1140w, 1310s, 1350vs, 1440w, 1520sh, 1600sb, 3060sb.
[$MoOBr_3$ 5-nitrophen]	715s, 730vw, 745w, 770wb, 830s, 900w, 965vs, 1145m, 1330sb, 1420m, 1500m.
[$Mo_2O_4Br_2$.(5-nitrophen)$_2$]	660w, 730sb, 760m,sh, 820m,sh, 840s, 910s, 960vs, 1120vw, 1160m, 1190w, 1210w, 1340vs, 1400w, 1430s, 1520vs, 1590w, 1640w, 3060wb, 3400wb

w = weak, m = medium, s = strong, vs = very strong, vw = very weak, sh = shoulder, wb = weak broad

TABLE 2

Compound	λ_{max} in mμ	ν (cm^{-1} $\times 10^{-3}$)	Molar extinction coefficient ϵ	Assignment
5-NitrophenH$_2$[$MoOCl_5$]	700	14.3	34	$^2B_2 \rightarrow {}^2E(I)$
	430	23.3	48	$^2B_2 \rightarrow {}^2B_1$
	310	32.3	20,3000	$^2B_2 \rightarrow {}^2E(II)$
	281	35.6	39,0600	$^2B_2 \rightarrow {}^2B_2(I)$
	239	41.8	33,7000	$^2B_2 \rightarrow {}^2E(III)$
[$MoOCl_3$ 5-nitrophen]	700	14.3	192	$^2B_2 \rightarrow {}^2E(I)$
	529	19 0	422	$^2B_2 \rightarrow {}^2B_1$
	322	31 10	7460	L→Mo Charge transfer
	265	37.70	18,300	$^2B_2 \rightarrow {}^2B_2(I)$
	225	44 40	22,100	$^2B_2 \rightarrow {}^2B_2(II)$
[MoO(OX) Cl 5-nitrophen]	531	18.9	274	$^2B_2 \rightarrow {}^2E(I)$
	319	31 4	5360	$^2B_2 \rightarrow {}^2B_1$
	264	37.8	12,910	L→Mo Charge transfer
	227	44.0	15,390	$^2B_2 \rightarrow {}^4B_2(I)$
5-NitrophenH$_2$[$MoOBr_5$]	670	14.9	240	$^2B_2 \rightarrow {}^4E(1)$
	471	21.3	5420	$^2B_2 \rightarrow {}^2B_1$
	414	24.1	31,120	$^2B_2 \rightarrow {}^2E(II)$
	370	27.0	29,800	$^2B_2 \rightarrow {}^2B_2(I)$
	280	35.7	229,000	$^2B_2 \rightarrow {}^2B_2(II)$
	247	40.4	225,800	$^2B_2 \rightarrow {}^2E(III)$
[$MoOBr_3$ 5-nitrophen]	747	13.38	180	$^2B_2 \rightarrow {}^2E(I)$
	542	18.44	1,158	$^2B_2 \rightarrow {}^2B_1$
	476	21.05	992	L→Mo Charge transfer
	395	25 31	3,262	$^2B_2 \rightarrow {}^2B_2(I)$
	264	37.87	22,520	$^2B_2 \rightarrow {}^2B_2(II)$
	224	44.65	28,920	$^2B_2 \rightarrow {}^2E(III)$

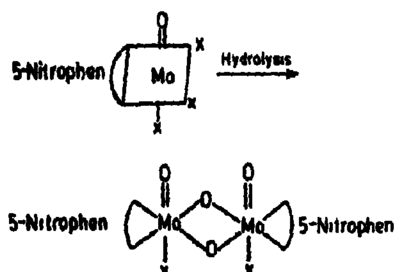
TABLE 3—REFLECTANCE SPECTRA IN SOLID STATE

Compounds	ν ($cm^{-1} \times 10^{-3}$)	Intensities	Assignment
[$Mo_2O_4Cl_2$ (5-nitrophen)$_2$]	13 7	w	$^2B_2 \rightarrow {}^2E(I)$
	17.5	m, sh	$^2B_2 \rightarrow {}^2B_1$
	23.0	s	L→Mo Charge transfer
	25 4	vs	$^2B_2 \rightarrow {}^2B_2(I)$
[$Mo_2O_4Br_2$ (5-nitrophen)$_2$]	13.8	w	$^2B_2 \rightarrow {}^2E(I)$
	16 6	m, sh	$^2B_2 \rightarrow {}^2B_1$
	22 9	s	L→Mo Charge transfer
	25.0	vs, b	$^2B_2 \rightarrow {}^2B_2(I)$

m = medium, sh = shoulder, w = weak, s = strong, b = broad, vs = very strong

Results and Discussion

The basicity of the substituted 1,10-phenanthroline i.e., 5-nitrophen is such that the dehydrohalogenation of the salts 5-nitrophen[$MoOX_5$] either in solvent or in solid state would be controlled only to the resultant stereospecific *cis*-nonelectrolytic [$MoOX_3$.5-nitrophen] products. The configuration of the non-electrolytes were determined from their mode of hydrolysis through the most expected *trans*-elimination reactions leading to the isolation of the dioxobridged compounds [$Mo_2O_4X_2$-(5-nitrophen)$_2$].



The presence of the oxobridges in the hydrolytic products were confirmed from their low magnetic moment values. In contrast to the identical cases[3,4] of $MoOX_3$.phen, all the attempts of isolating the $MoOX_3$.5-nitrophen in another stereochemical form failed.

The molybdenum oxygen bonding interactions have been treated for the ion [$MoOCl_5$]$^{2-}$ on the basis of a tetragonal structure with a short Mo-O bond[9]. The observed electronic spectra of the compounds containing the [$MoOX_5$]$^{2-}$ionic species taken in hydrogen halide acid medium are in good agreement with the spectra of the $(NH_4)_2[MoOCl_5]$ taken in 12 *M* HCl. It would therefore be reasonable to conclude that the salts so isolated evidently contain the oxopentahalo molybdate ion.

The presence of the d^1 electron in these compounds is evident from the magnetic data.

In explaining the spectra of the low symmetry non-electrolytic complexes, electronic transitions were reconciled with the standard assignments for previously synthesised similar compounds[12].

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Cobalt(II) Complexes of 5(3)-Methyl pyrazole-3(5)-Carboxamide

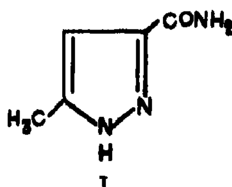
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The coordination behaviour of 5(3)-methylpyrazole-3(5)-carboxamide (MPA) has been reported by the isolation and characterisation of *bis*-complexes of Co(II), viz., $Co(MPA)_2X_2.nH_2O$ ($X = Cl, Br, I, ClO_4, NO_3, BF_4, SCN, \frac{1}{2}SO_4$; n=0, 2). The complexes possess a distorted octahedral structure as revealed from magnetic and electronic (diffuse reflectance and solution) spectral data. The ir data characterise the ligand as a neutral bidentate one coordinating through the amide oxygen and pyrazole-ring nitrogen (tertiary). The counter ion is preferentially coordinated in the solid state but is released in aqueous solution.

BIOCHEMICAL importance of heterocyclic acid amides and their derivatives is well documented[1]. The acid amide group itself is known to play a significant role in many biological processes. On the other hand, metal binding properties of acid amides are of special relevance to the chemistry of proteins which contain a number of amide linkages in their structures. Transition metal complexes of the amides of pyridine carboxylic acids have been studied[2]. As a part of our programme[3] of investigation of the coordination behaviour of pyrazole-based ligands, the present communication reports the isolation and physico-chemical characterisation of *bis*-complexes of cobalt(II) with 5(3)-methylpyrazole-3(5)-carboxamide (I, hereinafter abbreviated as MPA) which might have potential biological significance.



I

Experimental

(A) Preparation of the ligand :

The ligand, 5(3)-methylpyrazole-3(5)-carboxamide (MPA), was prepared by the reaction of liquor ammonia with an ethanolic solution of ethyl 5(3)-methylpyrazole-3(5)-carboxylate[4b]. The product on recrystallisation from ethanol melts at 174° (lit[4] m.p. 174°).

(B) Preparation of the Co(II) complexes :

(i) $Co(MPA)_2X_2.2H_2O$ ($X = Cl/Br/I/ClO_4/NO_3/BF_4/\frac{1}{2}SO_4$) : A solution of the hydrated cobalt(II) salt, $CoX_2.nH_2O$ (0.01 mole) in ethanol (aqueous ethanol in case of nitrate and fluoborate ; water in case of sulphate) was mixed with a solution of the ligand (0.02 mole) in the same solvent. The resulting reddish-pink solution was concentrated at water-bath temperature to a small volume and then cooled to room temperature when a pink compound with varying shades separated out. The compound, in each case, was collected on a filter, washed with ethanol (with water also for the sulphate complexes) and dried in a desiccator over fused calcium chloride.

(ii) $Co(MPA)_2(SCN)_2$: Ethanolic solutions of the hydrated cobalt(II) nitrate, $Co(NO_3)_2.6H_2O$, (0.01 mole) and potassium thiocyanate (0.02 mole) were mixed together and the precipitated KNO_3 was filtered off. The filtrate was evaporated to a small bulk and then filtered directly into an ethanolic solution of the ligand (0.02 mole). The resulting solution, after heating at water-bath temperature for 10 min, was cooled to room temperature ; the precipitated light pink compound was collected and dried as before.

(C) Elemental analyses and physico-chemical measurements :

Cobalt content of the complexes was estimated gravimetrically as anhydrous $CoSO_4$ except the perchlorate complex where the metal was estimated gravimetrically as cobalt mercurithiocyanate after decomposing the complex with conc. HNO_3 and H_2SO_4 mixture. Halogen was estimated as silver halide while sulphur was estimated as $BaSO_4$ in the usual manner. Nitrogen was determined microanalytically. The equivalent conductances, magnetic susceptibilities, electronic spectra (drs and solution) and ir spectra for the complexes were recorded as described earlier[5].

Results and Discussion

The results of elemental analyses of the complexes along with their colours and effective

TABLE 1—ANALYTICAL AND MAGNETIC MOMENT DATA FOR THE COMPLEXES

Complex	Colour	%Co		%N		% Anion(X)		μ_{eff} in B.M. (296°K)
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
$Co(MPA)_2Cl_2.2H_2O$	pink	14.16	14.20	20.19	20.30	17.04	16.88	4.52
$Co(MPA)_2Br_2.2H_2O$	pink	11.66	11.58	16 64	16 61	31.64	31.51	5.15
$Co(MPA)_2I_2.2H_2O$	brown	9 83	9 97	14.03	13 97	42.37	42.21	5.20
$Co(MPA)_2(ClO_4)_2.2H_2O$	reddish pink	10 82	10.80	15 44	15.32	13.03***	13.33	4.83
$Co(MPA)_2(NO_3)_2.2H_2O$	violet	12.56	12 41	23 88*	23.75	—	—	4.62
$Co(MPA)_2(BF_4)_2.2H_2O$	pink	11.36	11 50	16.20	16.11	—	—	4.84
$Co(MPA)_2SO_4.2H_2O$	pink	13.35	13 42	19 04	19.20	21.77	21 62	5.02
$Co(MPA)_2(SCN)_2$	light pink	13.65	13.76	26.34**	26 21	15.04****	15.12	4.89

* Including nitrogen present in nitrate,
** Including nitrogen present in thiocyanate,
*** Percentage of chlorine,
**** Percentage of sulphur

TABLE 2—ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Complex	State	Absorption maxima in kK (ϵ_{max})	ν_2(Calcd)	Dq	B	β
$Co(MPA)_2Cl_2.2H_2O$	Reflectance Methanol	8 2, 16 2, 19 5 19.2(21.6)	17.5	932	828	0.85
$Co(MPA)_2Br_2.2H_2O$	Reflectance Methanol	9.6, 15.0, 17 4sh, 20 2 17 2(27 9), 18.7(28 2)	20 3	1079	786	0 81
$Co(MPA)_2I_2.2H_2O$	Reflectance Methanol	9 4, 13 6, 16.8sh, 20.5 16.9(31.4), 18 9(30.9), 25.0(101 5)	20 2	1080	807	0.83
$Co(MPA)_2(ClO_4)_2.2H_2O$	Reflectance Methanol	9.0, 18 3sh, 20 0 16 9(28.0), 18 5(24 5)	19 2	1017	811	0.84
$Co(MPA)_2(NO_3)_2.2H_2O$	Reflectance Methanol	9 0, 17.2, 18.8 16.9(62 8), 18.0(49.6), 21.0sh(20.0)	19.0	1002	801	0.82
$Co(MPA)_2(BF_4)_2.2H_2O$	Reflectance Methanol	8 8, 19 0sh, 20 0 19.6(16 4)	18 8	996	824	0.85
$Co(MPA)_2SO_4.2H_2O$	Reflectance Methanol	8.4; 15.8sh, 19.4 19 2(29.9)	17 9	952	808	0.83
$Co(MPA)_2(SCN)_2$	Reflectance Methanol	8.6, 15 8sh, 19.0, 20 0sh 16 1sh(11.4), 19.2(46.2)	18 4	976	770	0.75

magnetic moment values are given in Table 1. The complexes are fairly soluble in water and low-molecular weight alcohols. Molar conductance values of aqueous solutions of the complexes lying in the range 230-290 $ohm^{-1} cm^2 mole^{-1}$ indicate their ionic nature atleast in the aqueous solution. The room temperature magnetic moment values of all the present cobalt(II) complexes, except the chloride and the nitrate, fall within the range 4.8-5.2 B.M. expected for six-coordinate high-spin cobalt(II) complexes[6]. The low magnetic moment values for the chloride (4.52 B.M.) and the nitrate (4.62 B.M.) complexes suggest that they may have an orbital singlet ground state with a distorted octahedral environment[7].

The diffuse reflectance spectral data of the complexes with respective ligand field parameters are given in Table 2. The spectra, in general, consist of two main broad bands, one appearing in the region 9.6-8.2 kK and the other in 20.5-18.8 kK which may be recognised as $\nu_1[^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ and $\nu_3[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$ transitions in an average octahedral field[8]. The values of ligand-field parameters Dq, B and β (Table 2) calculated from the assigned band positions of ν_1 and ν_3 (in an idealised O_h symmetry) by means of known relations[9], suggest an average octahedral environment of Co(II) ion in these complexes[8]. The calculated ν_2 band positions obtained from the relationship $\nu_2 = \nu_1 + 10$ Dq, are found to appear, in most cases, much close to the observed ν_3 bands; a close scrutiny reveals that the ν_2 transitions remain practically unobserved in the spectra of most of the present Co(II) complexes [except in the spectrum of $Co(MPA)_2(BF_4)_2.2H_2O$] where the weak shoulder at ~19.0 kK may be taken as ν_2 as is also expected[10] from the weak nature and proximity of the $\nu_2[^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)]$ transition to a strong ν_3 band. Therefore, it is suggestive that the weak bands often appearing as shoulder on the low energy side of the ν_3 band might be due to the presence of low symmetry components in the ligand field. The broad asymmetric nature of the ν_3 band indicating superimposition of the different

components into a single one also supports the above proposition.

The electronic spectral data of the methanolic solution (pink) of the complexes indicate that there is no significant change in the stereochemistry of the complexes on dissolution. The spectra, in general, consists of a characteristic octahedral Co(II) band appearing in the region 19.6-18.5 kK which can be recognised as the ν_3 transition in O_h symmetry; appearance of this band at lower wave number compared to the solid suggests some degree of solvation[10]. Low values of molar extinction coefficients give additional support for the pesudo-octahedral environment in most of the complexes. The high ϵ values (50-60) observed for the nitrate and thiocyanate complexes may be due to a distortion from octahedral structure[8]. The high intensity band of $Co(MPA)_2I_2.2H_2O$ in methanol at ~25.0 kK (ϵ = 101) might be of charge transfer origin.

IR spectra : The ir spectral data of the present complexes when compared with the free ligand give positive indications of the donor atoms of the ligand molecule to the Co(II) ion. The most important ir bands of the free ligand appearing at 3360, 1670, 1570, 1420 and 670 cm^{-1} may be assigned to NH stretching vibration (hydrogen bonded), ν(C=O), ν(C=N) of the pyrazole ring, ν(C−N) of the amide group and in-plane deformation of the pyrazole ring, respectively.

The most remarkable change that occurs in the ir spectra of the metal complexes as compared to the uncomplexed ligand is the negative shift of the ν(C=O) by ~10-20 cm^{-1} and a positive shift of the ν(C−N) (of the amide group) by ~10-30 cm^{-1}. These data strongly point to the participation[8,11] of the amide oxygen atom in complexation since coordination through the amide oxygen atom would tend to increase the single bond character of the carbonyl group and the double bond character of the C-N group thereby decreasing the ν(C=O) and increasing the ν(C−N), respectively. A comparatively smaller negative shift of the ν(C=O) than those usually observed in reported amide metal complexes may be ascribed to some sort of hydrogen bonding effect[8].

Appreciable positive shifts of the ν(C=N) (by ~10-15 cm^{-1}) and the in-plane deformation (by ~10-30 cm^{-1}) of the pyrazole ring in the complexes compared to the free ligand suggest the tertiary ring nitrogen atom as a possible bonding site. This conclusion is in good agreement with the earlier observations[12] on the metal complexes of N-heterocycles and is also in conformity with the crystallographic studies of several pyrazole metal complexes[13].

The bands in the 3μ region are a bit complicated in the ir spectra of the complexes due to the presence of ν(O−H) bands arising out of the presence of water molecules in the species and no useful conclusion can be drawn. The sharp bands at ~970-990 cm^{-1} in the fluoborate and sulphate complexes could be recognised as the rocking mode of coordinated water molecules[14].

The mode of linkage of the counterion, viz., thiocyanate, nitrate, perchlorate, fluoborate and sulphate, has been inferred from the ir spectra of the metal complexes. The strong bands at 2100 and 780 cm^{-1} in the spectrum of $Co(MPA)_2(SCN)_2$ may respectively be attributed to the νC≡N and νC−S vibration of an N-bonded NCS group[10]. Coordination[15] of the nitrate ion to the metal in $Co(MPA)_2(NO_3)_2.2H_2O$ is established by the appearance of bands characteristics of a monodentate nitrate ion in C_{2v} symmetry, viz., the split components of ν_4 at 1370(s) and 1310 cm^{-1} (m) and ν_2 at 820 cm^{-1}(s). In the spectrum of $Co(MPA)_2(ClO_4)_2.2H_2O$, the ir band of the perchlorate group due to Cl-O stretching frequency is split into three components appearing at 1140(m), 1110(m) and 1080(s) cm^{-1}; the extent of splitting indicate the presence of coordinated perchlorate group[16]. Appearance of strong broad band covering the region 1100-1020 cm^{-1} and 1150-1050 cm^{-1} in the spectra of fluoborate and sulphate complex respectively indicate that fluoborate[17] and sulphate[18] ions retain their ionic character in the present Co(II) complexes. It appears, therefore, that the ligand 5(3)-methylpyrazole-3(5)-carboxamide acts as a neutral bidentate ligand coordinating to the Co(II) ion through the pyrazole ring nitrogen (tertiary) and the amide oxygen in forming distorted octahedral Co(II) species, $Co(MPA)_2X_2.nH_2O$ (n = 0, 2), where the anionic counterpart is preferentially coordinated.

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γ-Carbon Bonded Acetylacetonato Complexes of Pd(II)

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Bis(acetylacetonato) Pd(II) reacts with Lewis bases such as α-, β or γ- picolines to produce complexes of the composition [Pd(ac.ac) (γ-ac.ac)B] quantitatively where B is the nitrogen base. In these complexes, one of the chelating acetylacetone ligand is transformed into carbon bonded state which has been characterised by infrared and ^1H nmr spectra.

ACETYLACETONE is a versatile ligand, usually the anion coordinates[1] to metal ion through the oxygen atoms completing a six membered chelate ring. The unidentate linkage through the central carbon atom (γ-carbon atom) is also known for Pt(II)[2] and Pd(II)[3]. A terminal carbon bonded complex of the composition Pd(ac.ac).Cl(bpy)[4] has also been reported. In this complex, the acetylacetone moiety still has an acidic proton, and O,O'-chelation of it with other metal ions forming di- and tri-nuclear complexes has been described[5,6]. On the other hand the compound [Pd(ac.ac)-(γ-ac.ac)(Py)][3] containing central carbon bonded acetylacetone has the β-diketone in keto form, and hence the possible ketonic coordination [as reported for the ionic Pt(II) complex[7]] or anion coordination (by abstracting the proton) with other metal ions was being investigated in this laboratory. The aim also was to synthesise the *bis* γ-carbon bonded complex [as reported for Pt(II)[8]] using a strong nitrogen donor. As a result, though the *bis* γ-carbon bonded complex could not be formed, a uni-γ-carbon bonded complex with γ-picoline as the nitrogen base was prepared. During the course of these investigations the reaction of $Pd(ac.ac)_2$ with a number of other nitrogen bases were studied. Nitrogen bases such as 2, 6-lutidine, 2-chloro pyridine, 2-fluoro pyridine, 2,6-dichloro pyridine, quinoline and isoquinoline did not produce the desired carbon bonded complex probably for steric reasons or presence of electron attracting substituents. This communication reports the results of reactions of $Pd(ac.ac)_2$ with α-, β- and γ-picolines.

Experimental

$Pd(ac.ac)_2$ (0.25 g) was suspended in γ-picoline (3 ml) and the mixture was warmed to 80-100° till a clear solution was obtained. Petroleum ether (10 ml) was added to the solution and kept in refrigerator overnight. Yellow crystals were obtained which were recrystallised from benzene-petroleum ether, yield, 0.315 g (90%). An exactly similar procedure was used for preparing compounds with β-picoline and α-picoline. However, even the use of excess of γ-picoline and reaction under reflux did not produce the *bis* carbon bonded complex.

Analysis and physical measurements were done as reported earlier[6]. Analytical and ir spectral data are listed in Table 1 and nmr spectral data in Table 2.

Results and Discussion

The compounds have the composition [Pd(ac.ac)-(γ-ac.ac)B] where B is α-, β- or γ-picoline. They are soluble in acetone, methanol, dichloromethane, chloroform and benzene. Molecular weight determination of the γ-picoline compound in chloroform indicated it to be monomeric (M.W. Found 372, Calcd. 397).

Characteristic absorption bands in the carbon bonded complexes are listed in Table 1. ν(C=O) and ν(C=C) vibrations of O,O'-chelated acetylacetone appear in the 1500-1600 cm^{-1} region and the bands in the 1600-1700 cm^{-1} region, which were not observed for $Pd(ac.ac)_2$, can be unambiguously assigned to the ν(C=O) vibrations of carbon bonded acetylacetone ligand[9]. There are many bands due to coordinated picoline molecule, but characteristic band due to ring vibration was observed at 1613-1618 cm^{-1}. The strong band observed at ~550 cm^{-1} can be assigned to ν(Pd-C) and other strong band at ~450 cm^{-1} is attributed to ν(Pd-O). ν(Pd-N) was observed at ~335 cm^{-1} in all the complexes.

The existence of one oxygen bonded chelating and one carbon bonded acetylacetonate ligand in the complexes is clearly confirmed by proton nmr spectra listed in Table 2. NMR spectra of Pt(II) complexes of carbon bonded acetylacetonate ligand were extensively studied by Lewis and coworkers[10]. In the spectrum of γ-picoline compound four methyl proton signals are observed with intensity ratio of 1 : 1 : 1 : 2. The lowest field peak is assigned to the two methyl groups of the C-bonded

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TABLE 1—ANALYTICAL AND IR SPECTRAL DATA (cm^{-1})

Compound	C	Pd	N	γ-ac ac $\nu(C=O)$	O-bonded ac ac $\nu(C=O)+\nu(C=C)$	Picoline ring vib.	ν(Pd-C)	ν(Pd-O)	ν(Pd-N)
Pd(ac.ac)(γ-ac.ac)B where B is									
γ-picoline	48 1 (48.8)*	26 2 (26 77)	3.32 (3 52)	1670 1637	1567 1577	1618	538	458	333
β-picoline	48 26	26.48	3 45	1668 1635	1565 1575	1615	543	450	335
α-picoline	48.14	26.25	3 38	1668 1638	1563 1523	1613	540	450	380

* Calcd. values are in parentheses

TABLE 2—^{1}H nmr DATA, δ (ppm)

	O-bonded ac.ac		C-bonded ac.ac		γ-picoline	
	CH_3	CH	CH_3	CH	CH_3	CH
[Pd(ac.ac)(γ-ac.ac)(γ-pic)]	2 04(24) 1 92(24)	5.44(8)	2.2(49)	4 32(8)	2.44(24)	7.2-7.4(16) 8 6-8.8(16)
Pd(ac.ac)$_2$	2.07	5 43				
Acetylacetone(enol)	CH_3 = 2.0	CH = 5.56	OH = 10 56	[Ref. J. L. Burdelt and M. T. Rogers, *J. Amer. Chem. Soc.*, 1964, 86, 2105.]		

Intensity ratio in parentheses

acetylacetonate ligand, indicating the two methyl groups to be equivalent. The other two peaks of equal intensity at higher field are attributed to the two methyl groups of the chelating ac.ac ligand. Fourth peak is assigned to the methyl proton signal of γ-picoline. It has been well established for the Pt(II) complexes[8] that the methine proton of the carbon bonded ac.ac absorbs at higher field in comparison to that of the chelating acetylacetone. This assignment also holds good for Pd(II) complexes. On being coordinated, the methyl and methine proton signals of the γ-picoline molecule are also shifted to lower field region. These experimental observations confirm the preparation of some further examples of γ-carbon bonded ac.ac complexes of palladium(II).

The probable mechanism of the transformation of chelated ac.ac to the carbon bonded one, may involve the coordinating solvent (picoline) assisted partial rupture of M – O bond of one of the chelated ac.ac molecule, rotation of the unidentate ac.ac around M – O bond to recoordinate through the central carbon atom. It was also observed that palladium(II) does not form complex containing two C-bonded ac.ac ligand, probably because the existence of one chelate ring might be necessary to stabilise the carbon bonding of the other acetylacetonate ligand. Reactions of this complex has shown that Pd-C bond is not stable unlike the Pt-C bond in ionic Pt(II) carbon bonded ac.ac complex and Pt(II) complexes containing *bis* γ-carbon bonded acetylacetonate ligand have been isolated to justify it.

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Thermodynamic Study of M^{2+}-Noradrenaline Systems in Aqueous Solutions

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The interaction of noradrenaline, [1-(3,4 dihydroxyphenyl)-2-amino ethanol], with M^{2+} has been studied potentiometrically and the stepwise and the overall thermodynamic constants have been worked out.

NORADRENALINE is a direct acting catecholamine like adrenaline. It elevates the blood pressure in hypertensive states resulting from trauma, hemorrhage, central vasomotor depression and acute myocardiac infarction. For this function noradrenaline possesses a wider margin of safety between its pressor and toxic doses than does adrenaline.

Although noradrenaline complexes of many transition metals have been reported in the literature [1-7], the interaction of this drug with M^{2+} in solution has not been studied so far. In continuation of our attempt[8] to study interaction of catecholamines with M^{2+}, we report here the results of our studies with noradrenaline.

Experimental

All the reagents employed were of high purity. The sample of noradrenaline was obtained from Fluka, Switzerland. The preparation and standardisation of the metal ion and ligand solutions and other experimental details are the same as reported earlier[8].

Stoichiometry of the adducts formed was ascertained by potentiometric (*p*H) and conductometric titrations. Toshniwal conductivity bridge using dip-type conductivity cell (cell constant 0.42) was used for the conductometric studies, while 'Systronics' *p*H-meter, type 322, using the combined glass electrode and reading 0.025 *p*H units was used for the potentiometric study.

The stepwise and overall formation constants were calculated at three temperatures, 0, 25 and 37° and at a fixed ionic strength of 0.1 *M* with KCl. The experimental procedure consists in titration of the following thermostated mixtures of solutions with a 0.2 *M* alkali solution and recording the *p*H after each addition of 0.05 ml of the alkali :

i. Mixture (A) : 5 ml of 0.02 *M* HCl.
ii. Mixture (B) : Mixture (A) + 10 ml of 0.01 *M* noradrenaline solution.
iii. Mixture (C) : Mixture (B) + 5 ml of 0.002 *M* metal solution.

The ionic strength of the above solutions was maintained to 0.1 *M* by adding the required quantity of 1.0 *M* KCl solution, keeping the total volume at 50 ml with double distilled water.

The values of $\bar{n}_H$, $\bar{n}$ and pL^- were calculated using the Irving-Rossotti equations[10], and the values of the formation constants (log K_1, log K_2 and log β_2) were directly obtained from the formation curves. The refined values for the same were computed by the best least square fits and are recorded in Table 1.

TABLE 1—FORMATION CONSTANTS OF M^{2+}-NORADRENALINE COMPLEXES

μ = 0 1 *M* KCl

		log K_1	log K_2	log β_2
Be(II)	0°	8 53	3 40	11 93
	25°	7 95	3 10	11 05
	37°	7 25	3 05	10 30
Mg(II)	0°	6 18	1 64	7.82
	25°	5.16	2 14	7.40
	37°	5.16	2 03	7.19
Ca(II)	0°	5 67	1 38	7.05
	25°	5 11	1.41	6.52
	37°	4.74	1.04	5.78
Sr(II)	0°	4 48	1.08	5 56
	25°	4 42	1 00	5.42
	37°	4 30	0.87	5 27
Ba(II)	0°	4 42	0.62	5 04
	25°	3 97	0 52	4 47
	37°	3 46	0.56	4.01

The thermodynamic parameters computed for the reactions studied were free energy, enthalpy and entropy changes and have been calculated using the isotherm, the isobar and the Gibbs-Helmholtz's equations respectively at 25 and 37° and ionic strength of 0.1 *M* with KCl (Table 2).

The metal adducts of the drug were isolated from the solution and their composition was ascertained by the methods described earlier[8]. The percentage of nitrogen was determined by the modified micro Kjeldahl method[8b], while the quantity of water associated with the complex from the difference in weight obtained on heating the complexes above 110°. The physical properties of

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TABLE 2—THERMODYNAMIC PARAMETERS OF M^{2+}-NORADRENALINE ADDUCTS

		Free energy change Kcal/g mole			Enthalpy change Kcal/g mole			Entropy change Cal/deg/mole		
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G$ (Overall)	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_2$ (Overall)	ΔS_1	ΔS_2	ΔS_2 (Overall)
Be(II)	0°	10.26	5.28	15 46	—	—	—	—	—	—
	25°	10.41	5.66	15.79	8.64	2 72	11.12	5 9	14.9	20.8
	37°	9.85	5 63	15.79	13 18	2 80	15 90	−10 7	9 4	−1.4
Mg(II)	0°	6 50	3.28	9 0	—	—	—	—	—	—
	25°	6 62	3 28	9.47	5 21	2.68	7 89	4 7	2 0	6.72
	37°	6.60	2.86	9 46	5.76	5.97	11.70	2.7	−10 0	−7.3
Ca(II)	0°	6 10	2 76	8.86	—	—	—	—	—	—
	25°	6.00	2 81	8.81	6.85	2 23	9 05	−2.8	1.9	1.3
	37°	5.74	2.36	8 10	8.58	5 76	14 34	−9 1	−10.9	−21.9
Sr(II)	0°	5.30	2 01	7.31	—	—	—	—	–	–
	25°	5.30	2.06	7.36	4.62	1.50	6.12	2 2	0.9	3.1
	37°	4.94	2.04	7.98	−7 30	1.78	9.10	−7 7	0.8	−6.9
Ba(II)	0°	4.83	1.56	5.78	–	–	–	–	–	–
	25°	4.74	1 44	6.18	5.81	2 83	8 64	−3 6	−4 6	−17.0
	37°	4.43	1 43	5.86	7.74	2.51	10 25	−10.7	−3 5	−14.1

the compounds isolated and their analytical data are given in Table 3, along with the important ir frequencies (recorded on Perkin Elmer infrared spectrophotometer, model 237).

TABLE 3—ANALYTICAL DATA AND IMPORTANT FREQUENCIES OF M^{2+} COMPLEXES OF NORADRENALINE

Compound	Props	Metal%	N%	H_2O%	NH sec. bending	OH bending
Noradren	—	—	—	—	1640 vs 1610 vs 830 w	1360 s 1085 s 1285 w
$BeI_2.2H_2O$	Dirty yellow*	2.4 (2.61)**	8.21 (8.12)	5 03 (5.2)	1640 w 1610 w	1360 s 1075 s
MgI_2 $2H_2O$	Yellow brown*	6.0 (6.06)	7.0 (7.07)	9.0 (9.09)	1640 w 1610 m 825 m	1360 s 1250 s 1050 w
$CaI_2.2H_2O$	Reddish brown*	9 6 (9.7)	6.6 (6 8)	8.2 (8 88)	1640 s 830 w	1390 s 1260 s 1080 m
[S]$rI_2.2H_2O$	Dark brown*	19.12 (19.1)	6 0 (6 1)	7.74 (7 7)	—	—
[B]$aI_2.2H_2O$	Dark brown*	26.87 (26.97)	5 54 (5 5)	7.0 (7 1)	1640 w 830 w	1360 w 1270 m 1080 vs

* Soluble in water and alcohol, hygroscopic and decomposes before melting.

** Values in the parenthesis are the Calcd. values.

[Re]sults and Discussion

The coductometric and potentiometric (pH) [titr]ations clearly indicate formation of ML and [ML]$_2$ adducts between M^{2+} and adrenaline. The titrations show liberation of only one proton [dur]ing chelation of each molecule of noradrenaline. [Hen]ce, the complexation of two molecules of the [liga]nd with M^{2+} may be represented as follows :



$$M^{2+} + HL = ML^{+} + H^{+}$$



$$ML^{+} + HL = ML_2 + H^{+}$$

[wher]e,



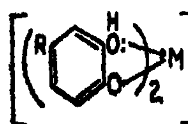
$HL = C_6H_3(OH)_2CH(OH)CH_2NH_2$.

Formation of 1 : 1 and 1 : 2 (M : L) adducts was also confirmed by the values of $\bar{n}$, which were in no case greater than 1.8.

An analysis of the formation curves indicates that noradrenaline follows the same pattern of addition to metal as was found for adrenaline[8] or as reported for aminoacids[9]. First, one atom of the metal combined with one molecule of noradrenaline. The 1 : 1 adduct thus formed did not appreciably combine with a second molecule of noradrenaline to give 1 : 2 complex until at least 80% of the 1 : 1 adduct had been formed. This indicates that the formation of the two species is independent of each other.

Complexation follows the standard pattern[10]. Comparison of stability constant data with corresponding adrenaline system suggests that stability of the noradrenaline systems is greater due to presence of primary amino group.

The analytical data for the isolated adducts gave the composition of these adducts to be $ML_2.2H_2O$, which is similar to that obtained for adrenaline adducts with these ions[8]. The ir frequencies of the isolated adducts indicate considerable change in the characteristic frequencies of phenolic $-$OH group in all the adducts, suggesting that the complexation might have taken place through the phenolic hydroxyl groups forming a five membered ring as suggested by Andrews *et al*[1]. Further, the potentiometric (pH) titrations indicated liberation of only one proton during the complexation of each molecule of the ligand. Hence, considering the coordination number of the metal ions=6, the following general structure may be given for the ML_2 adduct in confirmation of the structure reported earlier[8] :



The remaining two coordination positions are filled with two water molecules. This finds confirmation in the presence of the bands at frequencies 3600–3200 and 880–650 in ir spectra of these adducts (Table 3).

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Evaluation of the Mean Activity Coefficient of the Ions of Strong Electrolytes in Solutions whose Concentration varied from 0.001 *M* to 4 *M*

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In previous publications, the author has deduced an equation to account for the variation of the mean activity coefficient of the ions of strong electrolytes of 1 : 1 type in solutions of low concentrations, 0.001 to 0.1 m, by modifying the Debye-Hückel expression for k. This equation has been combined with that derived by Glueckauf to account for the effect of hydration on the activity coefficient of ions of the aforesaid type, using volume fraction statistics. The combined equation has been subjected to test using the data available in the literature on HCl, LiCl, NaCl, KCl and CsCl in the concentration range 0.2 m to 4 m and has been found satisfactory.

It follows from the treatment developed by Robinson and Stokes[1] and by Glueckauf[2,3] that in the case of aqueous solutions of strong electrolytes, the effects of (*i*) interionic attraction and (*ii*) of hydration on the mean molal activity coefficient, γ, of the ions in the region above 0.1 *M* may be represented by the following expression :

$$\log \gamma = \log \gamma^{el} + \log \gamma^{s} \quad .. \quad (1)$$

Robinson and Stokes[1] have identified $\log \gamma^{el}$ with the Debye-Hückel expression, $\frac{A(Z+)(Z-)\sqrt{I}}{1+Ba\sqrt{I}}$, and for $\log \gamma^{s}$ they have derived an expression using mole fraction statistics.

Denoting $\log \gamma^{s}$ by $\log \gamma^{vfs}$, and using volume fraction statistics, Glueckauf[2,3] derived an expression which, after neglecting some minor terms, may be written as

$$\log \gamma^{s} = \log \gamma^{vfs} = \frac{0.018\ mr\ (r+h-\nu)}{2.3\ \nu\ (1+0.018\ mr)} + \frac{h-\nu}{\nu}$$

$$\log (1+0.018\ mr) - \frac{h}{\nu} \log (1-0.18\ mh) \quad ... \quad (3)$$

where r = (apparent molar volume of electrolyte at m = 1 for 1 : 1 electrolyte)/(molar volume of water), h = hydration number and ν = the number of ions formed by a molecule. For $\log \gamma^{el}$, Glueckauf[3] also used the Debye-Hückel expression besides a function $X_{(m)}$, which becomes significant above 0.1 m. According to him upto m = 3, the $X_{(m)}$ function follows the empirical equation $X_{(m)} = -0.06\left[\frac{m}{1+0.5\ m}\right]^{2}$.

He also found[3], as suggested by Bjerrum, that when the concentration of the electrolyte was appreciably above 0.1 m, $\log \gamma^{el}$ could be replaced empirically by $-K\ m^{\frac{1}{3}}$ where K is a constant.

The values of γ calculated by using the equations of Robinson and Stokes and of Glueckauf have been found to agree well with the experimental data, but Glueckauf's equation based on volume fraction statistics has got some other advantages which have been acknowledged by Robinson and Stokes also. Therefore, the equation obtained by combining the expression for $\log \gamma^{el}$ deduced by the author with that for $\log \gamma^{vfs}$ deduced by Glueckauf has been used in this paper.

Deduction of the combined equation : In previous publications[4,5], by modifying the expression for k of the Debye-Hückel theory, the author has derived equations which can account for the variation of mean molar activity coefficient of the ions of strong electrolytes at low concentrations viz., 0.001 m to 0.1 m.

The equation for 1 : 1 electrolytes may be written as

$$\log\ y = -[(B)/(A)^{\frac{1}{3}}][C^{\frac{1}{3}} - C_{o}^{\frac{1}{3}}] \quad ... \quad (4)$$

$$= -[(B)/(A)^{\frac{1}{3}}](C)^{\frac{1}{3}} + a_{o} \quad .. \quad (4a)$$

In equation (4), B is a constant whose value can be calculated from theory, A represents the effective ionic diameter and C_{o}, which is a very small constant, may be interpreted to represent the concentration at which y becomes unity. In equation (4a), $a_{o} = [(B)/(A)^{\frac{1}{3}}](C_{o})^{\frac{1}{3}}$ and hence it is a small constant.

When the concentration of the electrolyte is low, $\log \gamma^{el}$ is to be identified with log y of equation (4) or (4a). For high concentrations, adopting the usual relation, $\gamma = \left[\frac{c}{md_{o}}\right] y$ it follows from equation

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TABLE 1—VARIATION OF MEAN ACTIVITY COEFFICIENT OF IONS WITH DILUTION AT 25°

Miscellaneous	2	3	4	5	6	7	8	9
HCl	m = c	0.001	0.002	0.005	0.01	0.02	0.05	0.1
Eqn. (4a) $B/(A)^{1/2}=0.287$ $(A)=(2.63)^2$ Å	Obs. y	0.965	0.953	0.929	0.905	0.876	0.830	0.794
$a_0=0.0086$	Cal. y	0.966	0.952	0.929	0.907	0.880	0.834	0.792
HCl	m	0.2	0.3	0.5	0.7	1.0	2.0	
Eqn (6)	C	0.1987	0.2975	0.4940	0.6890	0.9788	1.921	
$B/(A)^{1/2}=0.287$	Obs. γ	0.767	0.756	0.757	0.772	0.809	1.009	
r = 1.05 h = 5.84	Cal. γ	0.774	0.763	0.762	0.772	0.804	0.997	
LiCl	m	0.2	0.3	0.5	0.7	1.0	2.0	
Eqn. (6)	C	0.1987	0.2975	0.4940	0.6890	0.9788	1.921	
$B/(A)^{1/2}=0.263$ $(A)=(2.87)^2$ Å	Obs. γ	0.757	0.744	0.739	0.748	0.774	0.921	
r = 1.08 h = 5.60	Cal. γ	0.752	0.741	0.736	0.748	0.781	0.998	
NaCl	m = c	0.001	0.002	0.005	0.01	0.02	0.05	0.1
Eqn (4a) $B/(A)^{1/2}=0.265$ $(A)=[(2.85)^2]$ Å	Obs. y	0.965	0.952	0.927	0.902	0.871	0.819	0.774
$a_0=0.0118$	Cal. y	0.966	0.950	0.925	0.900	0.870	0.820	0.778
NaCl	m	0.2	0.3	0.5	1.0	2.0		
Eqn. (6)	C	0.1987	0.2975	0.4940	0.9788	1.921		
$B/(A)^{1/2}=0.265$	Obs. γ	0.734	0.710	0.682	0.658	0.671		
r = 1.03 h = 4.06	Cal. γ	0.727	0.703	0.676	0.654	0.682		
KCl	m = c	0.001	0.002	0.005	0.01	0.02	0.05	0.1
Eqn. (4a) $B/(A)^{1/2}=0.265$ $(A)=[(2.85)^2]$ Å	Obs. y	0.965	0.952	0.927	0.902	0.869	0.816	0.768
$a_0=0.011$	Cal. y	0.965	0.950	0.924	0.899	0.869	0.819	0.773
KCl	m	0.2	0.3	0.5	1.0	2.0	3.0	4.0
Eqn. (6)	C	0.1983	0.2965	0.4914	0.9689	1.883	2.744	3.553
$B/(A)^{1/2}=0.265$	Obs. γ	0.717	0.687	0.650	0.605	0.575	0.573	0.582
r = 1.4 h = 3.0	Cal. γ	0.714	0.685	0.648	0.602	0.573	0.575	0.592
CsCl	m	0.1	0.2	0.3	0.4			
Eqn (4a)	C	0.0993	0.1978	0.2955	0.3925			
$B/(A)^{1/2}=0.30$ $(A)=[(2.08)^2]$ Å	Obs. y	0.759	0.700	0.664	0.638			
$a_0=0.02$	Cal. y	0.761	0.700	0.661	0.632			
CsCl	m	0.5	1.0	2.0	3.0	4.0		
Eqn (6)	C	0.4886	0.9578	1.840	2.653	3.399		
$B/(A)^{1/2}=0.30$	Obs γ	0.606	0.544	0.496	0.479	0.474		
r = 2.3 h = 2.4	Cal. γ	0.603	0.545	0.495	0.478	0.474		

(4a), neglecting a_0, that :

$$\log \gamma^{el} = \log\left(\frac{c}{md_0}\right)y = -\left[(B)/(A)^{\frac{1}{2}}\right](C)^{\frac{1}{2}} + \log\left[\frac{c}{md_0}\right] \qquad (5)$$

where d_0 represents the density of the solvent.

Now substituting in equation (1) the values of $\log \gamma^{el}$ and $\log \gamma^{vis}$ as recorded in the equations (5) and (3) it may be written as

$$\log \gamma = -\left[(B)/(A)^{\frac{1}{2}}\right](C)^{\frac{1}{2}} + \log\left(\frac{c}{md_0}\right) + \frac{0.018\,mr\,(r+h-\nu)}{2.3\,\nu\,(1+0.018\,mr)} + \frac{h-\nu}{\nu}\log(1+0.018\,mr) - \frac{h}{\nu}\log(1-0.018\,mh) \ \ldots\ (6)$$

At 25°, B and d_0 in equation (6) are 0.624 and 0.997 respectively in aqueous solution.

In the following section of the paper, the validity of each of the equations (4a) and (6) has been subjected to test using preferably such electrolytes, the data on the mean activity coefficient of which at 25°, are available both in the low concentration range 0.001 to 0.1 m and the high concentration range 0.2 to 4 m.

Processing of data : The data on the mean activity coefficient of the ions of some 1 : 1 electrolytes in aqueous solution at 25° are recorded in Table 1. In column 1 of the table, under the head miscellaneous, are mentioned the electrolyte and the equation used and the values of the constants in the equation. For dilute solutions upto 0.1 *N* we have taken molar concentration C = m, molal concentration. For the concentrated solutions, C has

been calculated using the equation $C/m = d_0 - Am + Bm^2$ (vide Harned and Owen[6]). Cal. γ and Obs. γ represent the calculated and observed values of the mean activity coefficients. For C corresponding to m=1 an approximate value of 'h' is first found which yields γ of the right magnitude. The value of h is then adjusted by trial so as to yield values of γ in close agreement with the observed ones over as wide a range of C as possible.

For the dilute solutions of the electrolytes, the data on HCl, NaCl and KCl have been collected from Shedlovsky's paper[7]. The data on concentrated solutions of HCl, LiCl and CsCl have been collected from Robinson and Stokes book[1] (pp. 491-495, Tables 9-11), and those on NaCl and KCl have been collected from Harned and Owen's book[6] [p. 731, Table (12-3-1A)].

Discussion

It will be noticed from the data recorded in Table 1 that in the concentration range 0.001 to 0.1 m the calculated values of y agree well with those observed for the electrolytes HCl, NaCl and KCl, the data of which are available at 25° in the aforesaid concentration range. In the case of CsCl a few data are available at 25° in the concentration range below 0.1 m but the equation (4a) holds good upto 0.4 m, and above that equation (6) holds good.

At high concentrations recorded in Table 1, the agreement between the calculated and observed values of γ may be considered satisfactory upto 1.0 m for HCl, LiCl and NaCl, upto 3.0 m for KCl and upto 4.0 m for CsCl.

It may be pointed out that the value of (B)/(A) calculated by using equation (4a) in the low concentration range, where data are available, remain unchanged when equation (6) is used for calculating γ of the same electrolyte in the high concentration range.

It may be meantioned that the value of 'h' of an electrolyte calculated by using equation (6) differs somewhat from that calculated by Glueckauf[2,3]. The difference, however, is not much ; for example in the case of KCl, where the percentage difference is maximum, h=3.0 according to equation (6) and 2.58 according to Glueckauf[2,3].

This difference in the values of 'h' does not affect the approximately linear relationship between 'h' and $\frac{1}{r}$ (where r is the Pauling radius) observed by Glueckauf[2]. It only alters the slope of the straight line.

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Heat Capacity and Thermodynamic Properties of Some Mixed Fluorides

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Heat capacities (C_p) of some mixed fluorides, having the composition $KNi_xZn_{1-x}F_3$, where x=0, 0.49, 0.69, 0.85, were measured over the temperature range 80-300 K, using an isothermal calorimeter. $KNi_{0.85}Zn_{0.15}F_3$ and $KNi_{0.69}Zn_{0.31}F_3$ exhibited humps in their C_p vs T curves with maxima at 239.2±0.2 K and 190.0±0.2 K respectively, presumably corresponding to their Néel points. No anomalous behaviour in C_p was detected in $KNi_{0.49}Zn_{0.51}F_3$ and $KZnF_3$. Thermodynamic functions, such as entropy, enthalpy and Gibbs free energy were evaluated between 80-300 K.

To estimate magnetic contributions to heat capacity, two methods, namely, Debye-Einstein (DE) and corresponding states (CS), were employed to determine lattice heat capacity. The values of enthalpy of transition for $KNi_{0.85}Zn_{0.15}F_3$ and $KNi_{0.69}Zn_{0.31}F_3$ were found to be 213 (DE), 231 (CS) and 148 (DE), 168 (CS) cal/mol, respectively.

A problem in magnetochemistry, which has attracted considerable attention in recent years, is the variation of thermal and magnetic properties, especially in the region of the ordering temperature of a ferromagnet (T_C) or an antiferromagnet (T_N), as the system is diluted by substitution of a non-magnetic component. One of the interesting series of compounds has been '3d' metal double fluorides of the type KMF_3, where M=Mn, Fe, Co, Ni, etc. Since these compounds crystallize in the cubic perovskite structure, they are ideally suited for the study of 180° superexchange in the antiferromagnetically ordered state below room temperature. Many workers[1] have measured the magnetic susceptibility and reported on the antiferromagnetism of these compounds, the Néel temperatures being about 88 K ($KMnF_3$), 114 K ($KCoF_3$), 275 K ($KNiF_3$) and 243 K ($KCuF_3$), respectively. Corresponding heat capacity peaks were reported by us[2] at 83.3 K, 109.5 K, 253.5 K and 233.2K respectively.

The present communication deals with heat capacities and thermodynamic properties of $KNi_xZn_{1-x}F_3$ (x=0, 0.49, 0.69, 0.85) compounds over the temperature range 80-300 K. This study was undertaken to investigate the effect of random substitution of paramagnetic nickel by diamagnetic zinc ions on the Néel temperature and to estimate thermodynamic parameters, including those associated with magnetic order-disorder transition.

Experimental

The samples for calorimetric measurements were prepared by the method reported in the literature[3]. Analysis of X-ray powder diffraction photographs indicated that the solid solutions, $KNi_xZn_{1-x}F_3$, possess cubic perovskite structure at room temperature, the respective lattice constants being 4.04Å (x=0), 4.02Å (x=0.49), 4.00Å (x=0.69) and 3.98Å (x=0.85). The values of x, obtained from chemical estimation of nickel using the conventional dimethylglyoxime method, were in good agreement with the results of X-ray analysis.

The details of the construction and operation of the isothermal calorimeter employed in the heat capacity measurements have been described elsewhere[4,5].

Results and Discussion

Smoothened heat capacity curves have been depicted in Fig. 1. The average scatter of the observed C_p values from their own mean was about 1-2%.

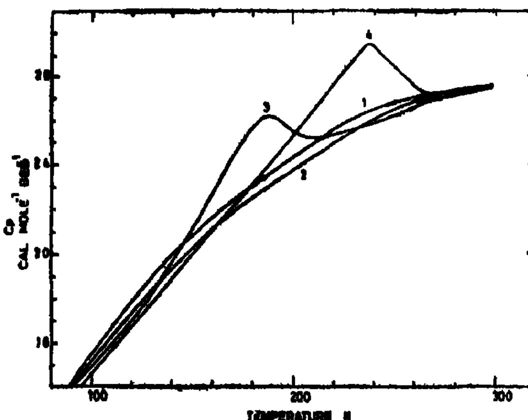


Fig. 1. Heat capacities of $KNi_xZn_{1-x}F_3$ compounds.
1. $KZnF_3$ 2. $KNi_{0.49}Zn_{0.51}F_3$
3. $KNi_{0.69}Zn_{0.31}F_3$ 4. $KNi_{0.85}Zn_{0.15}F_3$

$KNi_{0.85}Zn_{0.15}F_3$ and $KNi_{0.69}Zn_{0.31}F_3$ exhibited humps in their C_p vs T plots with maxima at

239.2 ± 0.2 K and 190.0 ± 0.2 K, respectively, presumably corresponding to their Néel points (T_N). Since $KNiF_3$ reveals a peak[4] in C_p at 253.5 K, it is evident that magnetic interactions are weakened by random replacement of paramagnetic nickel by diamagnetic ions, whereby the length of the interacting chain is decreased. On the otherhand, magnetic studies on the same compound have shown[5,6] a peak in magnetic susceptibility (χ) at about 280 K. The difference between T_N and the temperature at which the maximum in χ occurs needs an explanation. $KNiF_3$ crystallizes in a cubic perovskite structure which is an extremely close-approximation of a 3-dimensional nearest neighbour only Heisenberg system. It can, therefore, be assumed that the anisotropy is very small. Dipolar contributions cancel because of the cubic symmetry which is retained also at low temperatures[7]. Further, the above argument is strengthened by the findings of Yamaguchi and coworkers[8] who showed that the next nearest neighbours interactions are only 5×10^{-3}th of the nearest neighbour interaction. One, therefore, expects from this model a difference of the order of 10% between T_N and the temperature at which the maximum in χ occurs. Our experimental finding satisfactorily confirms this theoretical prediction[9]. Further, the presence of magnon or magnon-type of excitations in the paramagnetic region has been predicted by Marshall[10] on the basis of the spin-wave theory. Even in the absence of long-range ordering about T_N, there will exist regions of correlated spins as a consequence of the short-range order.

No anomalous behaviour was detected in $KNi_{0.49}Zn_{0.51}F_3$ and $KZnF_3$. Considering the excitations of a 3-dimensional disordered Heisenberg antiferromagnet within the framework of a Greens function, Janes and Edwards[11] estimated the critical concentration, C, of spins at which the system ordered magnetically to be equal to 0.34. Therefore, on the basis of our heat capacity measurement, $KNi_{0.49}Zn_{0.51}F_3$ should reveal magnetic ordering below 80 K which is the lower limit of temperature measurements.

Thermodynamic properties such as entropy, S°, enthalpy $H^\circ - H^\circ_0$, and Gibbs free energy $(G^\circ - H^\circ_0)/T$, were evaluated between 80-300 K. For this purpose, extrapolation of C_p values below 80 K was made using the following functions :

$KNi_{0.85}Zn_{0.15}F_3$:

$D(96/T)+2E(260/T)+2E(505/T)(80-130\text{ K};\ \pm1\%)$

$KNi_{0.69}Zn_{0.31}F_3$:

$D(95/T)+2E(260/T)+2E(480/T)(80-300\text{ K};\ \pm1\%)$

$KNi_{0.49}Zn_{0.51}F_3$:

$D(93/T)+2E(265/T)+2E(480/T)(80-200\text{ K};\pm0.5\%)$

$KZnF_3$:

$D(90/T)+2E(270/T)+2E(425/T)\ (80-300\text{ K};\ \pm1\%)$

The respective values at a few selected temperatures have been listed in Table 1. The values for x=0.49 are likely to be in error, if a magn transition exists below 80 K.

TABLE 1—THERMODYNAMIC FUNCTIONS OF KNi_xZn_{1-x} COMPOUNDS (1 cal = 4.184 J)

T/K	C°_p cal/K mol	S° cal/K mol	$H^\circ - H^\circ_0$ cal/mol	$-(G^\circ - H^\circ_0)$ cal/K mol
		$KNi_{0.85}Zn_{0.15}F_3$		
80	12 0	(9.25)†	(432)†	(3.85)†
100	14.5	12.20	698	5.23
200	25.2	25 60	2688	12.15
300	27 5	36.60	5449	18.64
		$KNi_{0.69}Zn_{0.31}F_3$		
80	12.1	(9.35)†	(4.36)†	(3.89)†
100	14 7	12 95	705	5.80
200	25 4	26.44	2808	12.40
300	27.5	37.05	5433	18.94
		$KNi_{0.49}Zn_{0.51}F_3$		
80	12.3	(9 39)†	(434)†	(3.97)†
100	14 9	12 43	707	5.86
200	23 8	25 89	2701	12.39
300	27 5	36 44	5314	18.78
		$KZnF_3$		
80	12.6	(9 64)†	(445)†	(4.08)†
100	15.4	12.76	726	5 50
200	24 3	26 57	2768	12.73
300	27.6	37.25	5413	19.21

† Figures within the parenthese are extrapolated values.

The following methods were employed to estimate the lattice heat capacity and entropy and then the corresponding magnetic contributions in $KNi_xZn_{1-x}F_3$ (x=0.69, 0.85) compounds :

(i) *Debye-Einstein (DE) method :* A combination of Debye-Einstein functions, used for extrapolation of heat capacities below 80 K, was assumed to represent the lattice heat capacity when extended upto 300 K. It was further assumed that $C_p\sim C_v$. The magnetic heat capacity and the associated enthalpy of transition (ΔH) could then be determined.

(ii) *Corresponding states (CS) method :* Since the system $KNi_xZn_{1-x}F_3$ crystallizes in the cubic perovskite structure and formula weights of the concerned compositions do not differ widely, it may be assumed that the vibrational contributions to entropy and heat capacity of these compounds obey a law of corresponding states. Then, S (lattice) = ϕ (T/θ) and C_p (lattice) = (T/θ) ϕ' (T/θ) where ϕ is the same function for $KZnF_3$, $KNi_{0.69}Zn_{0.31}F_3$, $KNi_{0.85}Zn_{0.15}F_3$ and θ is a characteristic temperature, different for each compound. The method of calculation was analogous to that employed by Stout and Catalano[12] for isostructural MF_2 compounds. The values of r ($KNi_xZn_{1-x}F_3$, S) evaluated around 300 K were found to be 0.94 and 0.92 for x=0.69 and 0.85, respectively. The values of enthalpy of transition for x=0.69 and 0.85 were determined to be 146 (DE), 168 (CS) and 213 (DE), 231 (CS) cal/mol, respectively.

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Heat Capacity and Thermodynamic Properties of Sr_2MoCoO_6 and Sr_2MoNiO_6

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The heat capacity (C_p) of the system Sr_2MoMeO_6 ($Me=Co^{2+}, Ni^{2+}$) has been studied in the temperature range of 290-580 K. Anomalies in heat capacity were observed with a slight hump around 417 K and 452 K for Sr_2MoCoO_6 and Sr_2MoNiO_6, respectively. Since no structural, magnetic or dielectric transitions exist in the relevant temperature range, these transitions appear to be of electrical in origin.

COMPOUNDS with the general formula ABO_3 which crystallise in perovskite like structures have been extensively studied in view of their dielectric, magnetic and thermal properties. The perovskite structure has been found susceptible to wide variation in compositions from the ideal ABO_3 formula by substitution of either A or B with cations of different valency states. Investigations in this direction have been made on compounds of the type[1,2] A_2MMeO_6. X-ray, magnetic and dielectric studies[3] have been reported on Sr_2MMeO_6 ($M=Mo^{6+}, W^{6+}$ and $Me=Co^{2+}, Ni^{2+}$). However, little information is available on the thermal properties of the above system. Besides, the transition temperature values reported by various techniques were found to differ appreciably. Since the calorimetric data are more precise and are hardly affected by trace impurities, heat capacity measurments of Sr_2MoMeO_6 ($Me=Co^{2+}, Ni^{2+}$) were made to examine their type and temperature of transition. The results are discussed in this communication.

Experimental

The requisite amounts of AnalaR grade constituent oxides (except SrO which was weighed in the form of $SrCO_3$) were mixed by milling under acetone in an agate mortar and air dried. The dried mixtures were prefired below 1273 K in a platinum dish, ball milled and again fired for 4-6 hr between 1473 and 1573 K in air.

The final products were analysed by X-ray diffraction using CuK_α radiation ($\lambda=1.5418$ Å) and were characterised as single phase with tetragonal symmetry at room temperature (Sr_2MoCoO_6: a=3.94 Å and c=3.97 Å; Sr_2MoNiO_6: a=3.92 Å and c=3.95 Å) by comparison with ASTM data file. No extra lines due to any of the constituent oxides were detected within the sensitivity of the method.

The heat capacity (C_p) of the samples was measured in an adiabatic calorimeter which was calibrated using α-Al_2O_3 and ThO_2 as standards. Comparison of the observed data with NBS values indicated[4] the accuracy to be about ± 2% while the average scatter of the experimental values from their own mean was ± 1.5%. The measurements were done in the temperature range 290-580 K. In the neighbourhood of transition, shorter intervals of temperature (about 2°) were taken to study the detailed shape of the curve.

Results and Discussion

The experimental molar heat capacities were determined in the same chronological order as measured, to facilitate estimation of temperature increments in the measurements. Appropriate corrections were made for curvature to yield true differential heat capacities. Anomalies were observed with a slight hump around 417 K for Sr_2MoCoO_6 and around 452 K for Sr_2MoNiO_6, respectively (cf Fig. 1). The molar heat capacities, entropy and enthalpy of these compounds are given in Table 1.

In compounds crystallising with perovskite like structure, the co-existence of magnetic and dielectric dipole ordering has been reported and the transition might arise due to magnetic (antiferro-para), ferroelectric (ferro-para) or structural (tetragonal-cubic) transitions.

The magnetic ordering in these compounds can be accounted for on the basis of indirect exchange interaction of the type Me–O–M–O–Me, as

* For correspondence.

TABLE 1—THERMODYNAMIC FUNCTIONS OF STRONTIUM MOLYBDENUM COBALTATE AND NICKELATE

Temperature	Sr_2MoCoO_6			Sr_2MoNiO_6		
	C_p	$H_T - H_{298K}$	$S_T - S_{298K}$	C_p	$H_T - H_{298K}$	$S_T - S_{298K}$
K	J/mole.degK	J/mole.	J/mole.degK	J/mole.degK	J/mole.	J/mole.degK
300	108 6	217	0.72	103.9	207	0.69
350	114 0	5786	17.9	108.4	5510	17.0
400	121 0	11610	33.5	112.8	11045	31.8
450	119.6	17769	47.9	127.5	16890	45.6
500	123 1	23836	60.7	119.4	22890	58.2
550	125 6	30053	72.5	122.3	28940	69.7

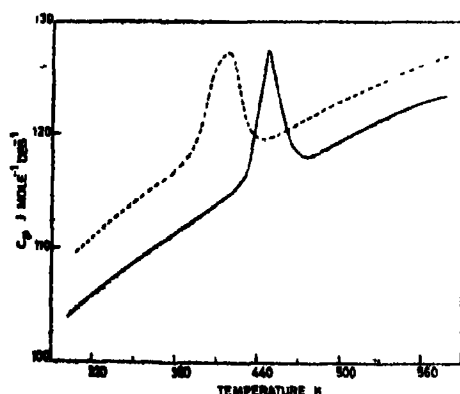


Fig 1. Heat capacity (C_p) of Sr_2MoCoO_6 and Sr_2MoNiO_6
·· Sr_2MoCoO_6
- -- Sr_2MoNiO_6

elucidated by Blasse[5], the respective Néel temperatures being 60 K for Sr_2MoNiO_6 and 34 K for Sr_2MoCoO_6. The susceptibility of Sr_2MoNiO_6 indicated a peak at 71.5 K which was attributed[3] to the onset of antiferromagnetic ordering and another at 503 K to structural transformation (tetragonal-cubic). Thus the transition temperature of 452 K for Sr_2MoNiO_6, observed in our studies, does not correspond to the reported value for the magnetic transition. It appears, therefore, that the anomalies in the heat capacities are not due to a magnetic transition.

Dielectric studies of these compounds indicated[8] the absence of anomalies arising from ferroelectric origin in the relevant temperature ranges.

From X-ray studies, the structural phase transition temperatures were reported[1] to be 503 K and 593 K for Sr_2MoNiO_6 and Sr_2MoCoO_6, respectively. These values are higher compared to our heat capacity peaks (452 K for Sr_2MoNiO_6 and 417 K for Sr_2MoCoO_6). These compounds may be thought of as derived from $SrTiO_3$ by substitution of Ti^{4+} by Mo^{6+} and either Co^{2+} or Ni^{2+}. It has been reported[6] that $SrTiO_3$ undergoes a structural transition from tetragonal to cubic at 110 K. But heat capacity measurements showed[7] no anomaly around this temperature. Substitution of Ti^{4+} by Ni^{2+} or Co^{8+} and Mo^{6+} having almost the same ionic radii may be expected to lead to a phase transition similar to that observed in $SrTiO_3$. Thus, heat capacity anomalies do not seem to correspond to structural phase transitions.

In view of the above, the possibility of the transition being electrical in origin may now be considered. The electrical conductivity measurements[8] indeed showed a break in the activation energy around 454 K for Sr_2MoNiO_6. This is in close agreement with our value of 452 K. It is believed that a similar explanation can be offered for the heat capacity peak in Sr_2MoCoO_6 although, as far as the authors are aware, no electrical conductivity data have been reported in the literature.

In conclusion, it may be stated that heat capacity anomalies were observed in Sr_2MoNiO_6 (at 452 K) and in Sr_2MoCoO_6 (at 417 K), respectively. These transitions are presumably electrical in origin, since the electrical conductivity of Sr_2MoNiO_6 also behaves anomalously around 454 K, while no structural, magnetic or dielectric anomalies exist in the relevant temperature ranges.

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First Dissociation Constant of Phosphoric Acid at a Number of Temperatures

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The pK_1 values of H_3PO_4 from 273.15 to 323.15 K have been recalculated from Nims as well as Bates data with the help of modified Davies equation. The difference in the pK_1 values has been largely reconciled. At 308.15 K, pK_1 has also been measured using Na-salt instead of K-salt. There is almost no difference in the values of pK_1 found. Bates had come to the conclusion that cells similar to Nims, where $m_{KH_2PO_4} : m_{HCl}$ lie between 1 and 3, or when pH is <3.0, do not give accurate pK_1 values. Using modified Davies equation, cells with pH values <3.0 gave reliable pK_1 values.

THERE are only a few reports on the determination of pK_1 of phosphoric acid at a number of temperatures by e.m.f. method using cells without liquid junction potential. Nims[1] determined pK_1 of phosphoric acid using cell (C−1) with three series of solutions having

$$(Pt)H_2 \mid KH_2PO_4(m_1), HCl(m_2), AgCl \mid Ag \qquad (C-1)$$

$m_1/m_2 = 2.071$, 3.102 and 3.079 and μ between 0.01 and 0.10 mol kg^{-1}. He used equation (1) to get pK_1 at 273.45, 288.65, 298.15, 310.65 and 323.15 K, where $\mu = m_1 + m_H$.

$$-\log m_H - \log\left(\frac{m_1}{m_2 - m_1} - 1\right) + 2A\sqrt{\mu} = pK_1 + B\mu \qquad (1)$$

Here B is an empirical constant whose value differed with the ratio $m_1 : m_2$.

Bates[2] used the same cell (C−1) and determined pK_1 from 273.15 to 333.15 K in steps of 5 K using five series of solutions having $m_1/m_2 = 1.2414$, 1.2683, 1.5581, 2.1840 and 6 and μ lying between 0.02 to 0.4 mol kg^{-1}. He defined a term pwH given in equation (2).

$$p\text{wH} = -\log \gamma_H.\gamma_{Cl}.m_H = \frac{(E-E^\circ)F}{2.3026\,RT} + \log m_{Cl} \qquad (2)$$

So pK_1 is given by eqnation (3).

$$pK_1 = p\text{wH} + \log\frac{m_{H_3PO_4}}{m_{H_2PO_4}} + \log\frac{\gamma_{H_2PO_4}.\gamma_{Cl}}{\gamma_{H_3PO_4}} \qquad \ldots \quad (3)$$

$$\text{where, } \left.\begin{aligned} m_{H_3PO_4} &= m_2 - m_H \\ m_{H_2PO_4} &= m_1 - m_2 + m_H \end{aligned}\right\} \qquad (4)$$

For use in equation (4) the value of m_H was obtained either from a provisional dissociation constant and applying the law of mass action and a method of successive approximation, or from pwH using equation (2). Since it is not possible to obtain an exact value of $\gamma_H.\gamma_{Cl}$, Bates defined an apparent m_H, namely m_H' and assumed that at low μ, $m_H = m_H'$ and is given by equation (5).

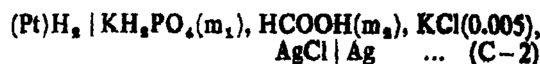
$$-\log m_H' = p\text{wH} - \frac{2A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad \ldots \quad (5)$$

So, apparent log K_1 or log K'_1 is given by equation (6).

$$pK'_1 = p\text{wH} + \log\frac{m_2 - m'_H}{m_1 - m_2 + m'_H} \qquad (6)$$

The values of pK_1 were plotted against μ, and the intercepts of the plots at $\mu = 0$ gave pK_1. Values of pK_1 thus obtained differed with the series used. This led Bates to conclude that accurate values of pK_1 could not be determined when $1 < m_1/m_2 < 3$ and $pH < 3.0$.

Bates then worked with cell (C−2). Using two



$$(Pt)H_2 \mid KH_2PO_4(m_1), HCOOH(m_2), KCl(0.005), AgCl \mid Ag \quad \ldots \quad (C-2)$$

series of solutions having $m_1/m_2 = 5$ and 8 and a different method of calculation he determined pK_1 of phosphoric acid from 273.15 to 333.15 K in steps of 5 K.

The values of pK_1 thus found by Bates differ from the pK_1 values of Nims [obtained with cell (C−1) using a different method of calculation] by 0.024 at 298.15 K and 0.017 at 323.15 K,—the only two temperatures common to both the workers.

We have recalculated pK_1 from the e.m.f. data of Bates with cell (C−1) using modified Davies equation[3] to see whether accurate values of pK_1 could be obtained from his cell (C−1). We have

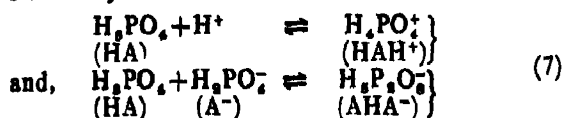
TABLE 1—pK_1 FROM BATES DATA (TAKING ALL THE SERIES TOGETHER)

Temp K	pK_1 given by Bates (from C – 2)	pK_1 recalculated from cell (C – 1) of Bates		β_1/mol^{-1} kg	
		Graphical	Statistical	Graphical	Statistical
273.15	2.056	2.057	2.056 ± 0.0022	0.260	0.26 ± 0.040
278.15	2.078	2.078	2.078 ± 0.0040	0.216	0.21 ± 0.077
283.15	2.088	2.091	2.091 ± 0.0080	0.192	0.19 ± 0.056
288.15	2.107	2.105	2.106 ± 0.0010	0.292	0.29 ± 0.031
293.15	2.127	2.126	2.125 ± 0.0018	0.310	0.31 ± 0.031
298.15	2.148	2.146	2.145 ± 0.0016	0.385	0.40 ± 0.053
303.15	2.171	2.169	2.169 ± 0.0010	0.370	0.37 ± 0.020
308.15	2.196	2.195	2.195 ± 0.0031	0.350	0.35 ± 0.068
313.15	2.224	2.218	2.218 ± 0.0031	0.390	0.39 ± 0.060
318.15	2.251	2.252	2.252 ± 0.0024	0.300	0.30 ± 0.065
323.15	2.277	2.280	2.279 ± 0.0018	0.260	0.26 ± 0.050

TABLE 2—pK_1 FROM NIMS DATA (TAKING ALL THE SERIES TOGETHER)

Temp. K	pK_1 given by Nims	pK_1 recalculated		β_1/mol^{-1} kg	
		Graphical	Statistical	Graphical	Statistical
298.15	2.124	2.153	2.152 ± 0.0015	0.400	0.40 ± 0.029
323.15	2.280	2.277	2.276 ± 0.0045	0.377	0.36 ± 0.002

also recalculated pK_1 from Nims data with cell (C – 1), using modified Davies equation to see how the recalculated values compare with Bates pK_1 values. Modified Davies equation is valid generally for $\mu < 0.1$ mol kg^{-1}. Also the equilibria considered by Edwards and Huffenon[4] viz.,



$$\begin{array}{llcl} & H_3PO_4 + H^+ & \rightleftharpoons & H_4PO_4^+ \\ & (HA) & & (HAH^+) \\ \text{and,} & H_3PO_4 + H_2PO_4^- & \rightleftharpoons & H_5P_2O_8^- \\ & (HA) \quad (A^-) & & (AHA^-) \end{array} \quad (7)$$

are not likely to occur below $\mu - 0.1$ mol kg^{-1}. We have therefore confined our recalculation to $\mu < 0.1$ mol kg^{-1}.

E.M.F. of cell (C – 1) is given by equation (8).

$$E = E^\circ - k \log m_H . m_{Cl} - k \log \gamma_H . \gamma_{Cl} \quad \ldots (8)$$

where, $k = 2.3026 \frac{RT}{F}$ and $E^\circ = E^\circ_{Ag/AgCl, Cl^-}$. Using modified Davies equation and rearranging, we get equation (9).

$$\frac{E - E^\circ}{k} + \log m_{Cl} - \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu = -\log m_H \quad . \quad (9)$$

where, $\beta = \beta_H + \beta_{Cl}$ and $\mu = m_1 + m_H$.

In terms of pwH defined in equation (2), log m_H is given by equation (10).

$$\log m_H = \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}} - \beta\mu - p\text{wH} \quad . \quad (10)$$

Bates has recorded the pwH values obtained with his cell (C – 1). According to modified Davies equation the values of β will be the same as in the case of cell (C – 3).



$$(Pt)H_2 \mid HCl, AgCl \mid Ag \quad \ldots (C\text{-}3)$$

The values of β found from cell (C – 3) have been reported elsewhere[5]. Assuming an arbitrary value of μ and a value of A obtainable from literature[6] we get a value of m_H from both equations (9) and (10). This value of m_H gives a fresh value of μ. The iteration procedure is continued till we get a constant value of μ and m_H correct to a micromol kg^{-1}.

$$\text{Now, } \left. \begin{array}{l} m_{H_2PO_4} = m_1 - m_{H_3PO_4} \\ m_H \quad = m_2 - m_{H_2PO_4} \end{array} \right\} \quad (11)$$

Putting $K_{1(A)} = \frac{m_{H_2PO_4} \, m_H}{m_{H_3PO_4}}$ and $\gamma_{H_3PO_4} = 1$, we

$$\text{get, } \log K_{1(A)} - \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}} = \log K_1 - \beta_1\mu \quad \ldots \quad (12)$$

where $\beta_1 = \beta_H + \beta_{H_2PO_4}$

Plots of L.H.S. of equation (12) obtained from a recalculation of Bates data with cell (C – 1) taking all the ratios of $m_1 : m_2$ together are linear (with some scatter) whose intercepts at $\mu = 0$ give log K_1, and the slopes give β_1. pK_1 and β_1 have also been obtained by a least square analysis (statistically). Table 1 shows these results.

It will be seen from the table that the recalculated values of pK_1 using modified Davies equation agree within 0.003 units with the reported pK_1 values of Bates obtained with cell (C – 2). Only at 313.15 K the difference goes upto 0.006 units.

The plots of L.H.S. of equation (12) at 298.15 and 323.15 K obtained from a recalculation of Nims data using modified Davies equation are also linear whose intercepts give log K_1, and slopes give β_1. These values have been recorded in Table 2.

It will be seen that the recalculated pK_1 values of Nims agree with pK_1 values of Bates within 0.007 at both 298.15 and 323.15 K, the only two temperatures common to both workers.

TABLE 3—E.M.F. AND THE MOLALITIES OF IONS IN CELL (C—4) at 308.15 K

$m_{NaH_2PO_4}$ (m_1)	m_{HCl} (m_2)	E/abs volt	$m_{H_3PO_4}$	m_H	$m_{H_2PO_4}$ (x)	$\mu = m_1 + m_2 - x$	$\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}$
0.029374	0.010221	0.50052	0.022131	0.002978	0.007242	0.032353	$\bar{3}.801$
0.037003	0.012909	0.49250	0.027370	0.003275	0.009633	0.040279	$\bar{3}.796$
0.044512	0.015522	0.48620	0.032519	0.003529	0.011993	0.048042	$\bar{3}.794$
0.053307	0.018225	0.48087	0.037761	0.003744	0.014480	0.057052	$\bar{3}.792$
0.058896	0.020547	0.47685	0.042269	0.003920	0.016627	0.062816	$\bar{3}.791$
0.067638	0.023241	0.47297	0.047448	0.004069	0.019171	0.070708	$\bar{3}.786$
0.080348	0.028385	0.46625	0.056349	0.004385	0.023999	0.084734	$\bar{3}.779$
0.086705	0.031000	0.46303	0.060278	0.004572	0.026427	0.091278	$\bar{3}.778$

All concentrations and ionic strengths are in mol kg^{-1}.

TABLE 4—pK_1 AND β_1 AT 308.15 K

Cell	pK_1	β_1/mol^{-1} kg
(C−1) with KH_2PO_4 and hydrogen electrode (recalculated)	2.195±0.0032	0.35±0.068
(C—4) with NaH_2PO_4 and hydrogen electrode	2.187±0.0016	0.33±0.025

In modified Davies equation β should be independent of the composition of ionic atmosphere unless it is drastically changed. To see this we set up cell (C−4), given later, at 308.15 K only.

Experimental

$NaH_2PO_4.2H_2O$ (AnalaR, B.D.H.) was found to be 99.98% pure when analysed by standard method[7]. A G.R., S.M., sample of HCl was diluted with water to sp. gr. 1.10 and fractionally distilled. The middle fraction, free from bromide[8], was collected and analysed separately against pure $AgNO_3$ and pure borax by standard methods[9]. A stock solution of $NaH_2PO_4.2H_2O$ and HCl in the approximate molal ratio of 3 : 1 was prepared from which the experimental solutions were obtained by suitable dilution with double-distilled water. The stoichiometric concentrations were correct to one micromol kg^{-1}. All weighings were corrected for buoyancy. Preparation of electrodes, filling up of cells, thermostat, potentiometer assembly etc were as reported earlier[10]. The e.m.f. of the duplicate (C−4) cells agreed within 0.06 mV. The recorded e.m.f. values of Table 3 are the mean of the two readings after applying correction for barometric pressure, vapour pressure and bubbler depth[11].

Results and Discussion

The e.m.f. of cell (C−4), is given by equation

$$(Pt)H_2 \mid NaH_2PO_4(m_1), HCl(m_2), AgCl \mid Ag \quad \ldots (C-4)$$

(8), and equations (9) to (12) are valid in this case also. The experimental e.m.f. values after correction, and the L.H.S. of equation (12) are recorded in Table 3. Here $m_1/m_2 = 3$ approximately and the pH of the buffer < 3.0. The plot of L.H.S. of equation (12) against μ obtained with cell (C−4) is linear.

Table 4 records the pK_1 and β_1 values obtained by us from cells (C−4) and (C−1). It will be seen from Table 4 that pK_1 values obtained with cell (C−4) are within 0.008 units of that recalculated from Bates cell (C−1) though pH of the cell solutions are < 3.0. The values of β_1 in the two cases are within ± 0.02 mol^{-1}kg. Our experiment as well as recalculation indicates that modified Davies equation can fruitfully be employed to give accurate values of pK_1 even below pH 3.0 and both the cells (C−1) and (C−4) are capable of giving accurate pK_1 values.

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Cosolvency Studies of Polyethylene. Part—I : Lowering of Cloud Temperature in Cosolvent Mixtures

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Polyethylene, though quite insoluble in any single solvent at near room temperature, was earlier found to dissolve in a mixture of two non-solvents. A few such cosolvent pairs, including some new ones, have been studied in details with respect to cloud temperature and the existence of optimum solvent composition as judged by a maximum in intrinsic viscosity. The failure of Gee's criterion for cosolvency has been pointed out. The results have also been discussed, with only partial success, with respect to an equation derived by Deb and Palit, based on the thermodynamic approach of Scott. Probably, some kind of specific interaction and structure formation play an important role in such cosolvency.

A number ofc osolvents for the difficultly soluble polyethylene (PE) were reported in our previous communication[1]. This communication reports an extension of the above study to more samples (some fractionated) in five new cosolvent pairs with respect to variation of cloud temperature and [η] with solvent composition.

Experimental

Materials : The polyethylene samples D-H are from Union Carbide, USA and WSG-22, WNF-15 and RQ-161 were supplied by I.C.I. (India) to whom our thanks are due. All solvents, excepting CS_2, THF and C_6H_6 were of analytical grade and were not subjected to further purification but distilled under anhydrous condition before use. CS_2, THF and C_6H_6 were purified by standard[1,2] methods.

Fractionation of the polymer and measurement of cloud temperature in the cosolvent mixtures were carried out according to the methods stated earlier[1].

Determination of molecular weight : Molecular weights of the various polyethylene fractions were determined by measuring the osmotic pressures of their xylene solutions at 60° in a Hewlett-Packard 501 high speed membrane osmometer using 0.08 membrane with the help of the following equation

$$\left(\frac{\pi}{C}\right)_{c\to 0}=\frac{RT}{\bar{M}_n} \qquad (1)$$

(the symbols have the usual significance)

Estimation of methyl groups (per 1000 methylene) of the fractionated polymer : The estimation of $-CH_3$ groups in the polymer samples was done by ir spectroscopy from the ratio of absorptions due to methyl and methylene groups with the help of suitable samples, with known percentage of methyl groups, used as standards. For all the compounds studied, fractionated or unfractionated (experimental and standard), a sharp peak was observed at 1370 cm^{-1} with a shoulder at 1390 cm^{-1}. The spectra of the standard samples (D, E, F, G) showed that there is a correlation between the number of the methyl groups per 1000 CH_2 and the ratio of the absorptions at 1370 and 1390 cm^{-1}. Plotting of A 1370/A 1390 against the number of methyl groups gives a straight line and this plot was used for estimating the number of methyl groups per 1000 CH_2 in the experimental samples. The spectra were recorded as KBr pellets in Perkin-Elmer Infracord 137 spectrophotometer with NaCl optics.

Measurement of intrinsic viscosity : Intrinsic viscosities were calculated using the equation

$$\eta_{sp}/c=[\eta]+k'[\eta]^2c \qquad (2)$$

where the solution viscosities were determined by measuring the flow times in Ubbelohde dilution viscometer for which the kinetic energy corrections are negligible.

Results and Discussion

Minimum cloud temperature $(T_c)_{min}$: In our previous preliminary work[1] xylene-CS_2 (1) was reported to be the most efficient cosolvent pair followed by cyclohexane-CS_2 (2). The work has been extended to five other cosolvent pairs, viz., toluene-CS_2 (3), benzene-CS_2 (4), chloroform-CS_2 (5), carbontetrachloride-CS_2 (6) and tetrahydrofuran(THF)-CS_2 (7). We were compelled to use CS_2 as the second component as we are yet to find another solvent with such powerful codissolving action on PE. Thiophene was found to be a very poor substitute for CS_2. Further, CS_2 with

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TABLE 1—CHARACTERISTICS OF POLYETHYLENE SAMPLES STUDIED

Polymer Designation	**Polymer crystallinity %	Melt index	Density gm/ml	$\bar{M}_n \times 10^{-3}$	$CH_3/1000\ CH_2$*
WSG-22	50	70.0	0.918	21.0	40[a]
WNF-15	54	7.0	0 919	28.0	—
RQ-161	51	data not available	data not available	24 – 28	—
D	64	3.5	0.918	31.0	30*
E	67	3.5	0.922	33.00	25*
F	61	23	0 914	25	35*
G	58	300	0.910	12	40*
H	42	$>10^4$	0.885	4	60*
FRACTIONS					
1	data not available	data not available	0.918	136.0	25[a]
2	,,	,,	,,	47.40	28[a]
3	,,	,,	,,	46.40	36[a]
4	,,	,,	,,	25.10	37[a]
5	,,	,,	,,	20.38	38[a]
6	,,	,,	,,	19.14	39[a]

* Estimated from density ,
** % Crystallinity for all samples being supplied by manufacturers ,
[a]Estimated from ir studies (vide experimental).

TABLE 2—$(T_c)_{min}$ OF CS_2-CO-SOLVENT SYSTEMS

Samples	THF °C	$CHCl_3$ °C	CCl_4 °C	Xylene °C	Cyclohexane °C	Benzene °C	Toluene °C	$(T_c)_{min}$ Cyclohexane TCE °C
WSG-22	17.0(50)*	19.0(45)	26.0(40)	26.5(25)	28.0(45)	34.5(30)	38.5(40)	35.5(30)**
D	15.5(45)	18.0(45)	25.0(40)	27.0(25)	28.5(50)	34.5(30)	25.0(15)	45.0(30)
E		17.5(40)	24.0(45)	28.0(25)	29.5(50)	37 0(30)	39.5(25)	48 5(35)
F		17.5(45)	24.5(40)	24.0(25)	27.5(50)		39.0(25)	38.0(35)
WNF-15				39.0(45)			—	
RQ-161				38.5(20)			—	
G							25 (15)	
H	22.0(50)						39.5(25)	
FRACTIONS								
1		23.0(45)	—	—	—			
2	23.5(45)	32.0(50)	22.0(40)	25.5(20)	25 5(50)			
3	22.5(55)	28.0(45)	26.0(40)	28.5(25)	25 0(50)			
4	18.5(50)	17 0(40)	25 0(40)	26 0(20)	24 0(55)			
5	21.5(45)	24.0(45)	28.0(45)	27 5(20)	18.0(45)			
6	22 0(55)	18.5(45)	23 0(45)	27.0(20)	23.0(50)			

* figures in parentheses indicate % CS_2 by volume.
** figures in parentheses indicate % TCE.

pyridine, dioxane and chlorobenzene had no effect on lowering T_c, and in chlorobenzene precipitation results.

A few more unfractionated polyethylene samples, whose characteristics are shown in Table 1, were also included. WSG-22 of medium high molecular weight was selected for fractionation and the fractions were studied individually in cosolvent pairs No. (1), (2), (5), (6) and (7).

The highest fraction was found insoluble in all these cosolvent pairs near room temperature excepting $CHCl_3$-CS_2, but its supply being meagre, it could not be used for T_c studies.

The T_c values are summarized in Table 2 and a few typical T_c versus composition curves are represented in Figs. 1-4. The trend of the curves is more or less the same, there being a deepwell concave to the composition axis, whose minimum point is the optimum solvent composition (OSC) and the corresponding temperature is $(T_c)_{min}$. It may be noted that the minimum cloud temperature is often (vide Table 2) as low as in the twenties and in some cases even below it, for example in THF-CS_2 and $CHCl_3$-CS_2 with unfractionated PE.

It was found somewhat unexpectedly that some lower fractions sometimes are less soluble than the higher fractions (Table 2) ; for example, fraction 5 in CCl_4-CS_2 system has a $(T_c)_{min}$ of 28° whereas for fraction 2, the $(T_c)_{min}$ is 22°. Also, the unfractionated sample, WSG-22, has a $(T_c)_{min}$ as low as 17° in THF-CS_2, whereas the fractions derived

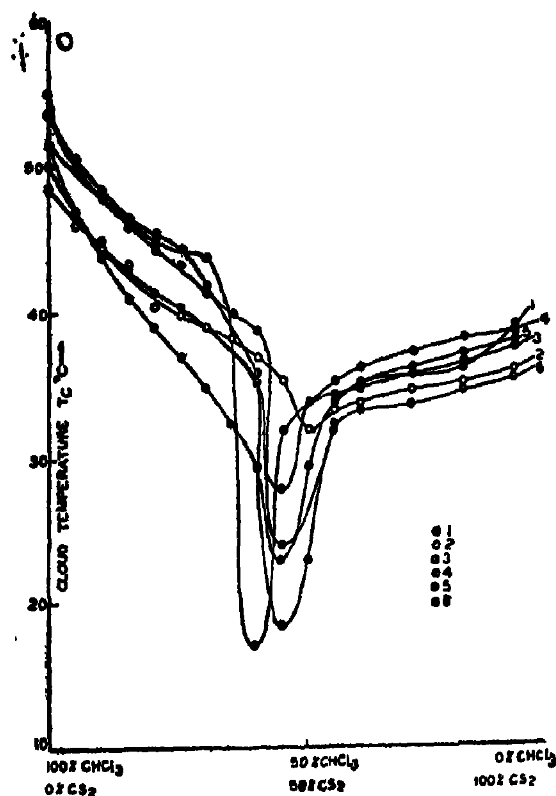


Fig 1. Plot of cloud temperature T_c of fractionated samples vs CS_2 content in $CHCl_3$.

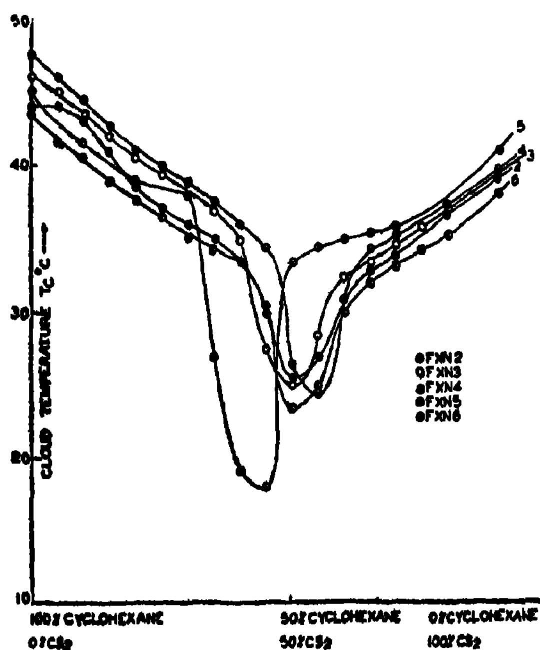


Fig 2. Plot of cloud temperature T_c of fractionated samples vs CS_2 content in cyclohexane.

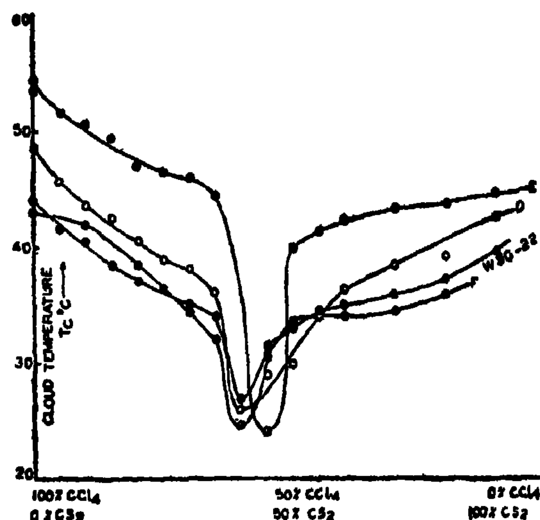


Fig 3. Plot of cloud temperature T_c of unfractionated samples vs CS_2 content in CCl_4.

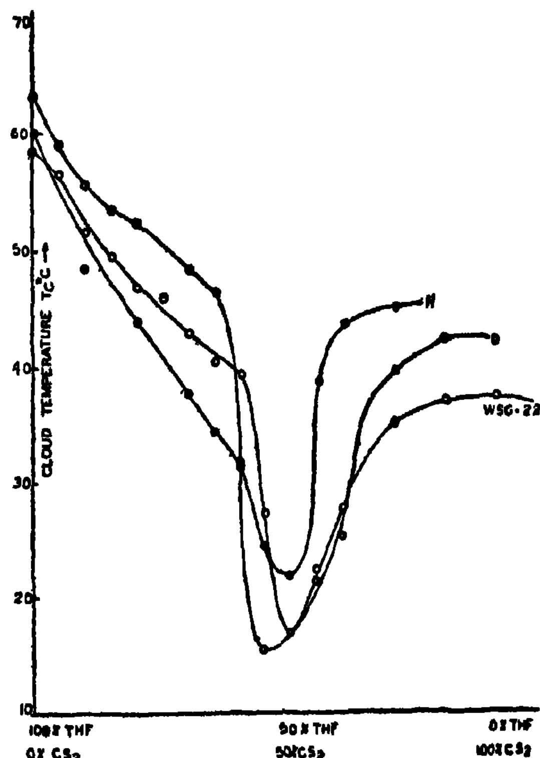


Fig. 4. Plot of cloud temperature T_c of unfractionated samples vs CS_2 content in THF.

from it do not exhibit such low $(T_c)_{min}$ values. This evidently means that (i) fractions are not identical in structure, and (ii) lower fractions have codissolving power for higher fractions—a fact well known in the varnish industry.

Variation of the optimum solvent composition : It is a remarkable fact that percent CS_2 in the

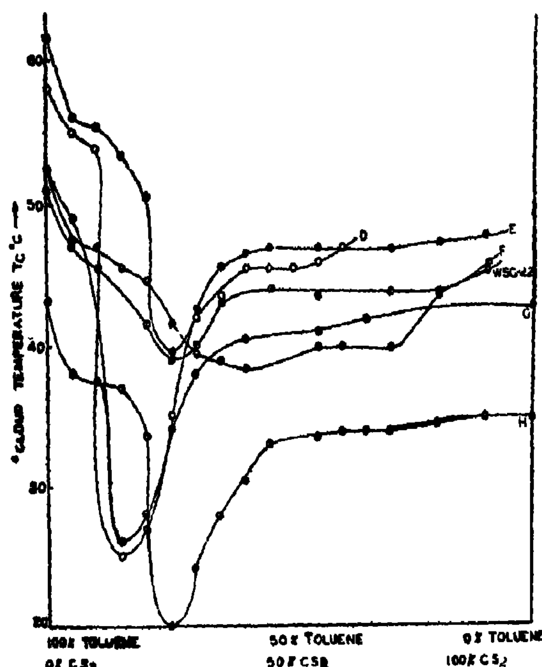


Fig 5 Plot of cloud temperature T_c of unfractionated samples vs CS_2 content in toluene.

optimum solvent composition in a given cosolvent pair is more or less the same (within ±5%) for all samples of PE. Out of 60 systems studied, only two exceptions were found in the case of WNF-15 in xylene-CS_2[1] and WSG-22 in toluene-CS_2 (Fig. 5; Table 2). In both these cases, the fall in T_c is small and the minimum is not well defined.

With respect to change of molecular weight, the OSC does not show any systematic change. This is probably expected because the polarity of the molecule remains essentially unaffected by a change in the degree of polymerization. The solubility of both the fractionated and the unfractionated polymer could not be correlated with the number of methyl groups in the sample, though it has been shown[8] that the solubility of polymers is highly sensitive to even small degrees of branching, in the sense that an isolated branched macromolecule is characterized by a higher degree of local concentration of segments than an isolated linear molecule of the same type and the same molecular weight in the same solvent.

Corroboration of OSC derived from $[\eta]_{max}$ *values as well as* $(T_c)_{min}$ *values:* Palit *et al*[8] and quite a few other workers[1,4,6-10] have shown that $(T_c)_{min}$ corresponds to a maximum in $[\eta]$ which is therefore the index of solvent power. This concept of agreement between $[\eta]_{max}$ and OSC, tested earlier[1], has been examined in other cosolvents[11].

Theoretical:

(i) *Solubility parameter and cosolvency:* It is evident that in our case δ plays hardly any role and the cosolvency is due to a specific interaction with CS_2. This is evident from the fact that CS_2 ($\delta=10$ in combination with many solvents with a wide range of δ values, which may be higher or lower than the δ value of polyethylene ($\delta=9$), exhibit co-dissolving power on PE. Hence, agreement with Gee's condition[12]

$$\delta_{(nonsolvent)1} < \delta_{polymer} < \delta_{(nonsolvent)2}$$

in a few cases may be regarded as merely fortuitous.

Even introducing the concept of energy density matching by using the relation

$$\delta_{mixture} = \phi_1\delta_1 + \phi_2\delta_2 \quad \ldots (3)$$

(where ϕ_1 and ϕ_2 are volume fractions) does not improve the matter to any remarkable extent because if δ_1 and δ_2 are both greater than $\delta_{polymer}$, merely giving weightage to them does not help the situation in any way.

(ii) *In the light of a more refined concept:* In order to examine how far Scott's formulation for a ternary system can be utilised to obtain an expression for the best solvent composition, Deb and Palit[13] proposed the following

$$(\delta_1-\delta_3)^2 v_1 - (\delta_2-\delta_3)^2 v_2 - (\delta_1-\delta_2)^2 \{(v_1-v_2)\phi_1^2 - 2v_1\phi_1 + v_1\} = 0 \quad (4)$$

where δ_is represent the cohesive energy density of the i-th components, v_1 and v_2 represent the molar volumes of the two liquids and the ϕs are the respective volume fractions.

The observed optimum solvent compositions for the different cosolvent systems have been compared with those obtained theoretically from the equation of Deb and Palit[13].

The agreement is only good to fair in many cases but hopelessly poor in benzene-CS_2, $CHCl_3$-CS_2 and THF-CS_2 where the theoretical prediction of ϕ_1 (volume fraction of solvent at the optimum) becomes unrealistic, i.e., greater than unity. However, it may be pointed out that this equation is quite unsuitable for such a test as it is highly sensitive to δ_3. We may therefore calculate δ_3 from our experimental data and compare it with the known value of $\delta_{polymer}$—a procedure also followed by Hilderbrand[14] in some cases during development of the δ concept owing to the same difficulty. The agreement at least for CS_2 systems may be considered good, the values ranging from 9 to 9.6 against the literature value of 9.0 (which is also an estimate). Thus, cosolvency studies may provide a method of determination of CED or δ of polymers. It appears that in such ternary systems, some kind of structure formation and microheterogeneity may be responsible for the unusual observations and the difficulty in theoretical interpretation.

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Cosolvency Studies of Polyethylene. Part—II : Viscometric Studies in Different Cosolvent Media

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Polyethylene, (PE), though insoluble in all solvents near room temperature, has been found to be soluble in a number of binary mixtures, one of which is CS_2. η_{sp}/c vs c plots for such systems have been found to be consistently of negative slope and in a few cases, this negative slope at low dilution is so pronounced as to appear like the 'upswing', typical of polyelectrolytes. The Mark-Houwink constants in a few such cosolvent pairs have been determined at a number of temperatures. Besides, the intrinsic viscosity-molecular weight relationship deduced theoretically by Palit has also been tested and found to be satisfactory. Further, the viscometric data have been utilised to calculate the unperturbed dimensions of PE (at different temperatures) by the use of Stockmayer-Fixman equation which agrees well with literature data. However, the viscosity data do not comply with the expectation of the theories of Kurata-Stockmayer-Roig or Flory-Schaefgen or Ptitsyn which may be due to a difference in composition of the solution layer and the bulk of the solution.

VISCOSITY studies of polyethylene (PE) in single solvents are rare and those in cosolvent media do not seem to exist. Some data on the constants of Mark-Houwink equation and molecular dimensions at high temperature in single solvents have been reported [1,2]. This communication reports a study of low density PE in a mixture of cosolvents. The cosolvents being a mixture of two nonsolvents with latent dissolving power such that the polymer dissolves in their mixture of suitable composition[3,4].

Experimental

Materials : The low density polyethylenes used in the present studies were the same as those obtained from I.C.I. (India) Ltd. and Union Carbide (U.S.A.) and used in an earlier study[4].

All solvents, excepting THF and CS_2, were of A. R. grade and were distilled before use. THF and CS_2 were subjected to further purification by standard methods[3,4].

Determination of molecular weight : Molecular weights of the different polymer fractions were determined by measuring the osmotic pressure of their xylene solutions at 60° in a Hewlett-Packard 501 high speed membrane osmometer. The molecular weights were calculated according to van't Hoff's equation,

$$\left(\frac{\pi}{c}\right)_{c\to 0}=\frac{RT}{\overline{M}_n} \quad (1)$$

where symbols are of usual significance. However, for the unfractionated polymer, the molecular weights supplied by the manufactures were used.

Measurement of intrinsic viscosity : Solution viscosity measurements were made at several concentrations with various cosolvent compositions and at different temperatures in an Ubbelohde dilution viscometer for which kinetic energy corrections are negligible. Intrinsic viscosities were obtained by extrapolation of the η_{sp}/c vs c plots to zero concentration (c, the concentration of the polymer solution being expressed in g/dl) in accordance with the Huggins' equation[5]

$$\eta_{sp}/c=[\eta]+k'[\eta]^2c \quad \dots (2)$$

where k' is a constant (Huggins' constant) for a series of polymers of different molecular weights in a given solvent.

Results and Discussion

Intrinsic viscosity and Huggins' constant k' : Viscosity results for fractionated and unfractionated samples soluble at 30° are presented in Tables 1 and 2. The η_{sp}/c vs c plots are linear but have a negative slope (vide Fig. 1 for representative plots) and so k' is negative. Normally, k' lies between 0.35 to 0.40. Hence our values cannot be interpreted in the light of Huggins theory.

Anomalous viscosity behaviour : Some of our η_{sp}/c vs c plots in solvents like a mixture of 50 : 50 cyclohexane-CS_2 show an unexpected behaviour of having an upswing as c approaches 0 (<0.1 g/dl). Such observations for polyvinyl chloride[6-14] have been attributed by Ohrn[15] to the adsorption of polymer on the walls of the capillary. This, however, cannot be true in our case as the viscosity measurements were made not only through dilutions inside the viscometer but were repeated by using

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TABLE 1—VALUES OF [η] (k' HUGGINS' CONSTANT) FOR DIFFERENT UNFRACTIONATED POLYMERS IN VARIOUS COSOLVENT MEDIA AT 30°

Sample		E	D	F	WSG-22	G	H
$\bar{M}_n \times 10^{-3}$		38	31	25	21	12	4
[η]dl/g				Xylene−CS_2			
in	75 . 25	1.15(−0.59)	1.07(−0.87)	0.90(−0.94)	0.86(−1.83)	—	0.19(−7.47)
	80 . 20	—	0 65(−1.66)	0.58(−1.90)	—	0.34(−1.99)	0.28(−15.83)
[η]dl/g				$CHCl_3$−CS_2			
in	50 . 50	0 59(−1 19)	0 56(−2 34)	0.58(−2.52)	0 49(−2 78)	0 40(−5.68)	0.29(−8.60)
	55 . 45	0.68(−1.09)	0.59(−1.71)	0.58(−1 81)	0.54(−2.31)	0 44(−4.03)	0.32(−5.05)
	60 : 40	0.68(−1.61)	0.52(−2.47)	0.52(−2.47)	0 49(−2.88)	0.39(−4.55)	0.28(−8.48)
[η]dl/g				CCl_4−CS_2			
in	55 · 45	0 74(−1.37)	0.59(−0.80)	0.60(−0.66)	—	0.37(−5.01)	0.16(−25.46)
	60 : 40	0.69(−1 1)	0.60(−3.12)	0.49(−0.70)	0 46(−4.65)	0 33(−6.49)	0.16(−24.46)
[η]dl/g				Cyclohexane−CS_2			
in	45 55	—	—	0 86(−0.86)	—	0.54(−2.31)	0 27(−10.83)
	*50 : 50	0 89*	0.83*	0 78*	1.56*	—	—
[η]dl/g				THF−CS_2			
in	45 55	—	0.60(−1 41)	0.40(−3.56)	0.30(−5.08)	0 36(−0.68)	—
	50 · 50	—	0.62(−1 25)	0.39(−5.58)	0.40(−3.84)	0 32(−6 17)	0.23(−14 24)
	55 · 45	—	0 68(−1.04)	0 41(−3.35)	0 38(−4 79)	0.22(−8.26)	0.19(−16 79)

* Exhibits anomalous viscosity, [η] values determined from Fuoss' equation (3)
The bracketted values are the corresponding k' values

TABLE 2—VALUES OF [η] (AND HUGGINS' CONSTANT k') FOR DIFFERENT FRACTIONATED POLYMERS IN VARIOUS COSOLVENT MEDIA AT 30°

Fraction		1	2	3	4	5	6
$\bar{M}_n \times 10^{-3}$		186 0	47 10	46 40	25 10	20.38	19.14
[η] dl/g				Xylene−CS_2			
in	75 . 25	—	0 51(−4 61)	0 41(−5 36)	0 21(−11.62)	0 16(−16 00)	0 15(−29.29)
	80 . 20	—	1 08(−0 68)	1 05(−0 91)	0 39(− 4.61)	0 19(−22 22)	0 16(−18 21)
[η] dl/g				$CHCl_3$−CS_2			
in	50 . 50	12 01(−0 16)	—	—	—	0 31(−9.13)	0 27(−9 86)
	55 45	—	—	1.26(−0.37)	—	0 35(−5 21)	0.32(−5.60)
[η] dl/g				CCl_4−CS_2			
in	55 45	—	0 56(−2 27)	0 54(−2 30)	0 46(−2.56)	0 38(−5.34)	0.34(−6.13)
	60 . 40	—	0 62(−2.19)	0 60(−2 50)	0 50(−2.65)	—	—
[η] dl/g				Cyclohexane−CS_2			
in	45 55	—	0 66(−0.40)	0 64(−0 78)	0 52(−1.18)	—	0.24(−2.19)
	*50 · 50	—	0 86	0.55	0.83	—	0 60
[η] dl/g				THF−CS_2			
in	45 55	—	—	1.12(−0.57)	—	—	0 34(−0.69)
	50 . 50	—	0.57(−0.78)	—	0.50(−2 39)	0 48(−2.59)	—
	55 . 45	—	0.83(−0.50)	—	—	0 41(−2.39)	—

* Exhibits anomalous viscosity, [η] values determined from Fuoss' equation (3)
The bracketted values are the corresponding k' values

in each case fresh solutions of different concentrations prepared outside and the same results were obtained.

Polyelectrolytes are well known to exhibit such upswing due to intramolecular coulombic repulsion[16] which evidently does not apply in our case. Ours is probably the result of pronounced negative slope of η_{sp}/c vs c curves. Our data can be formally treated by the equation proposed by Fuoss[17] for polyelectrolytes, i.e.,

$$\eta_{sp}/c = \frac{A}{1+Bc^{\frac{1}{2}}} \quad .. \quad (3)$$

(where A and B are constants) to obtain the value of [η] which cannot be obtained by normal extrapolation method. Plots of $(\eta_{sp}/c)^{-1}$ against $c^{1/2}$ give straight lines in all cases. The above anomaly (upswing), however, disappears with rise of temperature and shows the usual linearity with negative slopes. This sensitivity to high temperature may be due to structure formation at low temperature.

Intrinsic viscosity-molecular weight relationship :

(*i*) *Mark-Houwink equation :* The Mark-Houwink constants have been evaluated by plotting log [η] values reported in Tables 1 and 2 against log $\bar{M}_n$ in

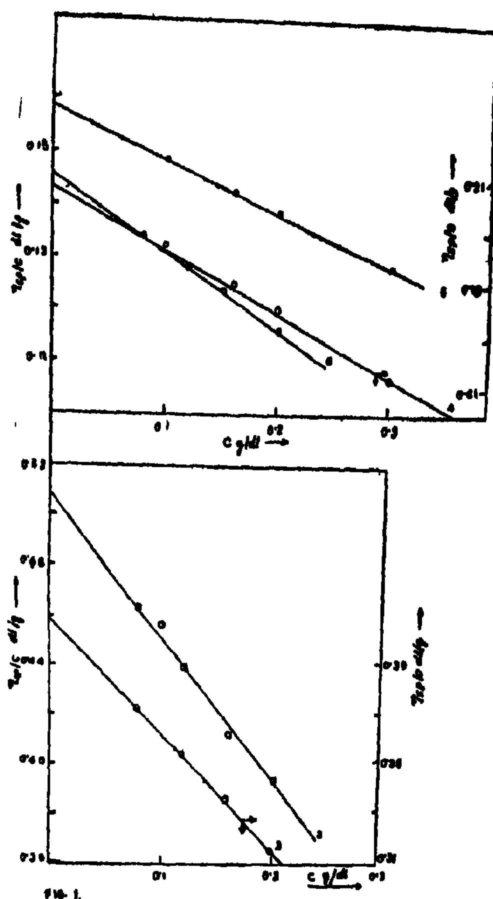


Fig. 1. Plot of viscosity vs concentration of fractionated samples in 75 25 xylene-CS_2 mixture at 30°

accordance with Mark-Houwink equation[18] $[\eta] = K'M^a$. Fairly good linear plots are obtained in all cases. The Mark-Houwink constants are reported in Table 3.

The K' values are normal for most polymers and are of the order of 10^{-4}. The 'a' value though theoretically expected to lie between 0.5 to 1, show an extensive range of values varying from as low a value of 0.2 to 0.9. Since Θ solvents have a value of 0.5, it appears that in such cosolvent media, the concept of Θ solvents does not apply unambiguously.

For the fractionated polymer in xylene-CS_2 (80 : 20), THF-CS_2 (45 : 55) and (55 : 45) and the unfractionated polymer in xylene-CS_2 (80 : 20), the 'a' values are close to 0.5 at 30° and so they may be considered to be under Θ condition. From consideration of the 'a' values and its temperature sensitivity, and low minimum T_c and less volatility and toxicity, we recommend xylene-CS_2 (75 : 25) and (80 : 20) at around 35° for routine use for viscometric molecular weight determination of PE by Mark-Houwink method.

(*ii*) *Effect of temperature :* We have determined the effect of change of temperature on $[\eta]$

Table 3—Mark Houwink's Constant for Fractionated and Unfractionated PE in Different Cosolvent Media at Various Temperatures

Cosolvent system	Cosolvent composition v/v	Sample	Temp. °C	k' × 10⁶	a
	75 : 25	fractionated	30	2798	0.27
	75 : 25	unfractionated	30	17.49	0.88
Xylene-CS_2	80 20	unfractionated	30	102	0.57
	80 . 20	fractionated	30	412	0.45
	,,	,,	34	3.29	0.88
	,,	,,	37	4.0	0.87
	50 · 50	unfractionated	30	1858	0.33
	50 . 50	fractionated	30	4.18	0.90
$CHCl_3$-CS_2	50 : 50	fractionated	34	1629	0.34
	,,	fractionated	37	1747 .	0.37
	55 : 45	unfractionated	30	1842	0.34
	,,	fractionated	30	60 5	0.64
	60 · 40	unfractionated	30	1271	0.36
	55 · 45	unfractionated	30	27.91	0.74
CCl_4-CS_2	,,	fractionated	30	13700	0.12
	60 40	unfractionated	30	80 46	0.64
	60 40	fractionated	30	26220	0.08
	,,	,,	34	28990	0.10
	,,	,,	37	17910	0 15
	45 55	fractionated	30	2755	0.29
Cyclohexane -CS_2	50 50	,,	30	1182	0 42
	,,	,,	34	10600	0.20
	,,	,,	37	4499	0.28
	45 55	unfractionated	30	5141	0 26
THF-CS_2	,,	fractionated	30	207	0.52
	50 50	unfractionated	30	1656	0.82
	,,	fractionated	30	25410	0.07
	55 45	unfractionated	30	478	0.44
	,,	fractionated	30	249	0.54
	,,	,,	34	1989	0.30
	,,	,,	37	2823	0.22

and the Mark-Houwink constants. Results are recorded in Tables 3 and 4, respectively. The constant 'a' is often found to be very sensitive to change of temperature. Sometimes, the value increases enormously with slight change of temperature, e.g., in xylene-CS_2, 'a' changes from 0.45 at 30° to 0.88 and 0.87 at 34° and 37°, respectively. This, however, is exceptional and in other systems, 'a' is generally found to decrease somewhat with temperature. Evidently, solvent power as judged by the values of 'a' has no simple relationship with temperature in such cosolvent systems.

Since the temperature dependence on $[\eta]$ according to Fox-Flory[19] treatment depends on the nature of the solvent and since our systems are rather close to Θ temperature (i.e., poor solvents) it is expected that $[\eta]$ should increase with increase in temperature. We have observed this in most cases and evidently the explanation seems to be that the expansion factor α increases with the increase in temperature.

A remarkably different case is the system THF-CS_2 where $[\eta]$ values decrease sharply over a small temperature interval, e.g., for fraction 2, the $[\eta]$ values are 0.83 at 30°, 0.67 at 34° and 0.403 at 37°, respectively. Such variations are very unusual and

Table 4—Effect of Temperature on the Intrinsic Viscosity (and Huggins' Constant k') of Fractionated PE in Different Cosolvent Media at their Optimum Solvent Compositions

Fraction		1	2	3	4	5	6
[η] dl/g				Xylene-CS_2 80 : 20			
at	30°	—	1.08(−0 68)	1.05(−0.64)	0.39(−4.61)	0.19(−22.22)	0.16(−18.21)
	34°	—	1.07(−1.71)	—	0.26(−4.61)	0.15(−28.68)	—
	37°	—	0 94(−0.24)	—	0.27(−6.31)	0.11(−34.45)	—
[η] dl/g				$CHCl_3$-CS_2 50 : 50			
at	30°	12.01(−0.16)	—	—	—	0.31(−9.13)	0.27(−9.86)
	34°	—	0.68(−2.65)	0.62(−3.10)	—	0.33(−2.15)	—
	37°	—	0.93(−1.06)	0.91(−1.20)	—	0.45(−3.02)	—
[η])dl/g				CCl_4-CS_2 60 : 40			
at	30°	—	0.62(−2.19)	0.60(−2.50)	0.50(−2.65)	—	—
	34°	—	0 87(−1.05)	—	0 64(−3.50)	0.58(−2.54)	—
	37°	—	1.11(−0.39)	—	0.71(−1,01)	0.60(−1.64)	—
[η] dl/g				Cyclohexane-CS_2 50 : 50			
at	*30°	—	*0.86	*0 55	*0.83	—	*0.60
	34°	—	0.91(−0.46)	—	0.67(−0 68)	—	0.61(−1.27)
	37°	—	1.19(−0.16)	—	0.77(−0.67)	—	0.64(−1.22)
[η] dl/g				THF-CS_2 55 : 45			
at	30°	—	0.83 (−0 50)	—	—	0.41 (−2 39)	—
	34°	—	0 67 (−1 97)	—	—	0 39 (−3 50)	—
	37°	—	0.403(−1.15)	—	—	0 254(−5.20)	0.247(−7.11)

* Exhibits anomalous viscosity, [η] determined from Fuoss' equation (3)

All bracketted values are k' values

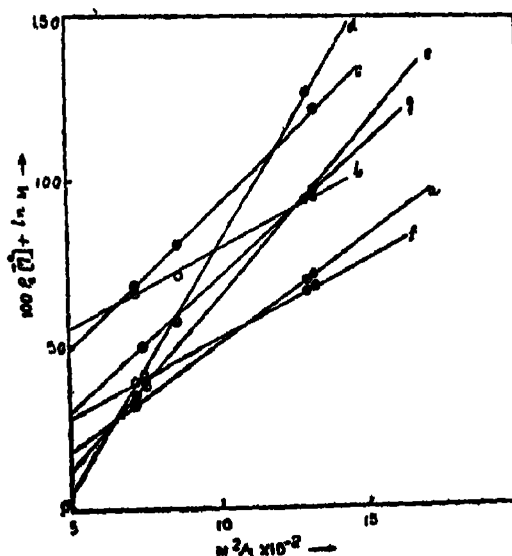


Fig 2 Palit-plots for the fractionated samples in different cosolvents at different temperatures

Cyclohexane-CS_2		Temp
(a)	45 : 55	30°
(b)	50 . 50	34°
(c)	50 : 50	37°
$CHCl_3$-CS_2		
(d)	55 45	30°
(e)	50 : 50	30°
(f)	50 : 50	34°
(g)	50 . 50	37°

should probably be attributed to the critical nature of differential solvation by the cosolvents.

(iii) The Palit relationship : A correlation between the intrinsic viscosity and molecular weight of polymers has been deduced by Palit[20]. The equation is given as

$$100\rho_0[\eta]+\ln M=K_1M^{2/3}+K_2 \quad .. \quad (4)$$

where ρ_0 is the partial specific density of the polymer at infinite dilution. A plot of $100\rho_0[\eta]+\ln M$ vs $M^{2/3}$ should be linear and our data fit quite well and the linearity is pretty good in all the cases of both fractionated and unfractionated polymers studied in all the five cosolvent systems at 30, 34 and 37° as is evident from Figs. 2 and 3. So, this relationship is not only applicable to simple solvents [21-23] but also to PE in cosolvents.

Determination of the unperturbed dimensions of PE in cosolvent media through the use of Stockmayer-Fixman equation : Since we were unsuccessful in determining Θ temperature by conventional methods, we took recourse to the following equation of Stockmayer and Fixman[24] to estimate the unperturbed dimension viz.,

$$[\eta]/M^{\frac{1}{2}}=K+0.51\,\phi\,BM^{\frac{1}{2}}$$
$$K=\phi(\langle r^{-2}\rangle_0\,;\,\phi\,M)^{3/2} \quad ... \quad (5)$$

The values of K obtained from the Stockmayer-Fixman plots are reported in Table 5. Exceptionally low values of K obtained for a few other systems are not reported herein.

For the unfractionated polymer, the value of $(\langle r^{-2}\rangle_0/M)^{\frac{1}{2}}$ for 55 : 45 CCl_4-CS_2 agrees excellently with those of Kurata and Stockmayer[25]. The interesting point is that they had carried

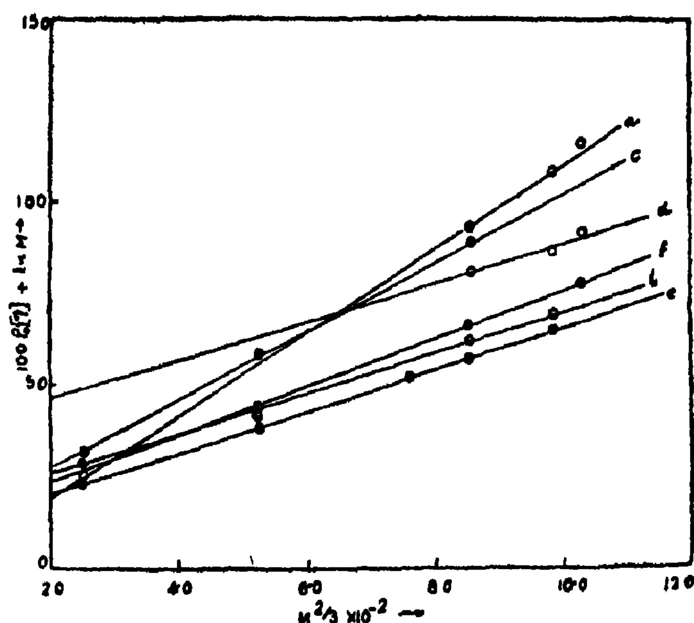


Fig. 3. Palit plots for the unfractionated samples in different cosolvents at 30°

Xylene-CS_2	(a)	75 : 25	(b)	80 20
Cyclohexane-CS_2	(c)	45 : 55	(d)	50 . 50
CCl_4-CS_2	(e)	60 40	(f)	55 : 45

TABLE 5—UNPERTURBED CHAIN DIMENSIONS FOR PE AT DIFFERENT TEMPERATURES AND IN DIFFERENT COSOLVENT MEDIA, CALCULATED FROM K VALUES (LITERATURE VALUE 950±40)[22]

Cosolvent system	Cosolvent composition		Sample	$K \times 10^5$	Temp. °C	$(\langle r^2 \rangle / M)^{\frac{1}{2}} \times 10^{11}$
Xylene-CS_2	75	25	unfractionated	180	30	767 94
	80	20	,,	360	30	1077.50
Cyclo-hexane-CS_2	45	55	unfractionated	340	30	1057 90
	,,		fractionated	415	30	1131 00
	50	50	unfractionated	480	30	1186 90
	,,		fractionated	470	34	1178 40
	,,		,,	300	37	1014 80
CCl_4-CS_2	55	45	unfractionated	230	30	928 82
	,,		fractionated	198	30	883.57
	60	40	unfractionated	180	30	855 95
	,,		fractionated	400	34	1114 60
	,,		,,	268	37	977.39
THF-CS_2	45	55	unfractionated	500	30	1203.10
	50	50	,,	420	30	1135.30
	,,		fractionated	480	30	1186 90
	55	45	unfractionated	325	30	1042 00
	,,		fractionated	92	30	648 35
	,,		,,	160	34	822 98
	,,		,,	180	37	855.95
$CHCl_3$-CS_2	50	50	unfractionated	420	30	1135 30
	,,		fractionated	82	34	658.62
	,,		,,	92	37	658 62
	55	45	unfractionated	495	30	1199.20
	60	40	,,	520	30	1220.40

out experiments at 100° and the present investigations were all carried out in the vicinity of room temperature. This is in accordance with the general concept that the unperturbed dimensions are independent of temperature and solvent typ[e] As is evident from Table 5 the values in general ar[e] slightly higher than those of the fractionate[d] polymers but there is a fair degree of consistenc[y] among the results.

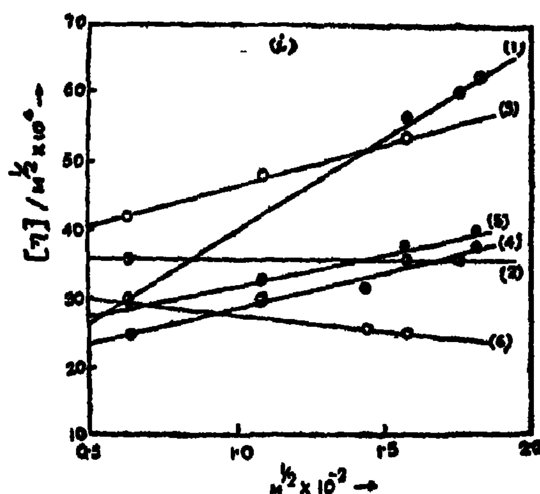
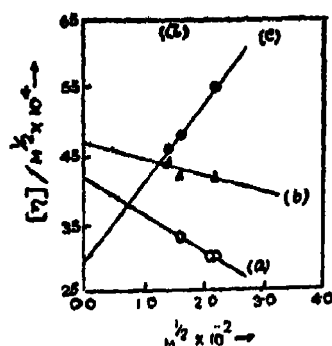


Fig. 4 Stockmayer Fixman plots for
(i) fractionated samples in cyclohexane-CS_2 at different temperatures

Cyclohexane-CS_2		Temp.
(a)	45 . 55	30°
(b)	50 : 50	34°
(c)	50 : 50	37°



(ii) unfractionated samples in different cosolvents at 30°

Xylene-CS_2	(1)	75 25	(2)	80 20
Cyclohexane-CS_2	(3)	45 55		
CCl_4-CS_2	(4)	60 40	(5)	55 · 45
THF-CS_2	(6)	55 45		

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Transition of Non-Faradaic Electrolysis to Faradaic Electrolysis by Change of Conditions

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Electrolysis of a sodium sulphate solution at various concentrations and current densities has been studied. Electrolysis of dilute solutions at low current is accompanied by anomalous (non-Faradaic) features. Keeping the current density constant at 1 mA/cm², non-Faradaic electrolysis becomes Faradaic as the electrolyte concentration is increased to 10^{-1} *N*. The electrolysis of 10^{-2} *N* solution is more or less Faradaic at current density, as low as 20 mA/cm².

ON elctrolysis of, say, a sodium sulphate solution at ordinary concentration and current density, Faradaic volumes of hydrogen at cathode and oxygen at anode are liberated. However, one of the present authors reported[1] a dramatic change in the results if the concentration is reduced to the region of 10^{-3} *N* or lower, and current density to near about 1 mA/cm². Firstly, considerably less gas is liberated (deficit). Secondly, V_C/V_A (ratio of the cathodic gas volume to the anodic) generally is higher than the theoretical value of 2 (cathode preference). Thirdly and most surprisingly, the cathode gas as well as the anode gas is an explosive mixture of hydrogen and oxygen (co-liberation). Electrolysis accompanied by such anomalous features is called non-Faradaic electrolysis as Faraday's law has no direct relevance to such results. The above reports were based on random studies. The present paper reports results of more careful and intensive study, particularly of the transition from non-Faradaic to Faradaic behaviour as effected by increase of concentration and/or current density using sodium sulphate as the prototype electrolyte.

Experimental

The cell used for our study is a simple *U*-tube connected to two gas burettes for collection of cathode gas and anode gas respectively as described in our previous publication[2]. Four such cells are connected in series so that the same current can pass through them. Each cell contains electrolyte solutions of different strengths from 10^{-4} *N* to *N*. A similar cell containing *N* K_2SO_4 is included in series to serve as a coulometer[3]. The cathode gas and the anode gas are collected in the gas burettes separately for each cell. Electrodes used are bright platinum foils (1 cm × 1 cm). Current is sometimes passed through a constant current apparatus (about 600 volts). Electrolysis is continued for several days (wherever necessary), so that quite a large volume of gas (more than 50 ml) gets collected. The liberated gases are then analysed by sending sparks through a sample with the help of a tesla coil and also by absorption in alkaline pyrogallol. The gases generally explode on sparking because the co liberation is more than about 7%. Most often, the co-liberation is much higher and hence the gases explode rather loudly and violently. Distilled water and 10^{-4} *N* solution had to be electrolysed separately i.e., not in series with others because of their high voltage requirement.

Each experiment is repeated several times in order to obtain the reproducibility of the results. Moreover, each solution has been electrolysed in all the four cells so that the cell to cell difference during electrolysis could be noted.

The results are not strictly reproducible. Thus, the results are not quite the same even if all the four cells are filled with the same solution and run at the same current density. But the variation is generally within a few percent provided the electrolysis is run over a long time so that at least 50 to 100 ml gas collects. There is also some variation from run to run. The first run is generally less non-Faradaic, if at all and things settle down to definite non-Faradaic features from second or third run onward. Therefore, we have generally neglected the result of the first run and averaged the results of the later runs. Fig. 1 shows the increase in co-liberation with run numbers for 10^{-3} *N* Na_2SO_4 at 1 mA/cm² current density. This kind of behaviour is probably due to the gradual increase in alkalinity and acidity at the cathode and the anode compartment, respectively. This is seen very strikingly with a not too dilute solution e.g., 10^{-2} *N* Na_2SO_4 at 20 mA/cm² current density and 40°. Very little co-liberation appears during the first hour of electrolysis but thereafter it becomes easily detectable and gradually increases with progress of electrolysis. However, when we used 10^{-2} *N* acid at anode and 10^{-2} *N* alkali at cathode to start with, co-liberation could be detected even after 10 min.

Results and Discussion

The main results are dicussed below. Since the trends and the distinctive features are better seen

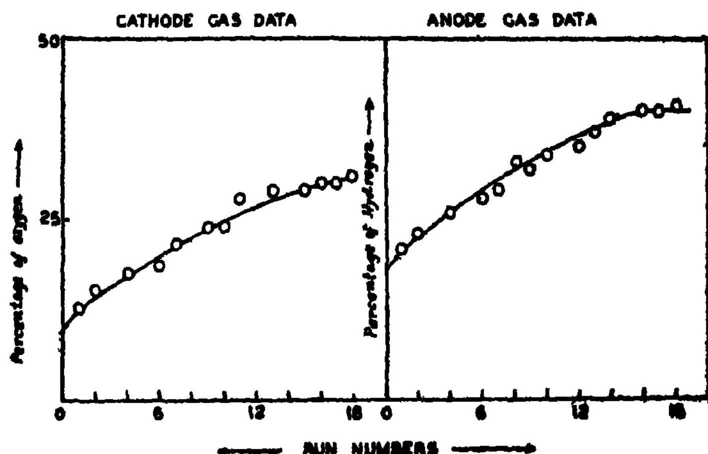


Fig 1. Results showing the increase in co-liberation with the progress of electrolysis of a 10^{-2} N Na_2SO_4 solution at the current density of 1 mA/cm^2.

graphically, we have prefered to present some of our typical results in graphical forms.

(i) *Effect of increasing concentration :* Starting with water i.e., zero concentration of electrolyte, we note that the current is rather small at the beginning due to the high resistance and it gradually increases to about 0.7 mA or a little more on prolonged electrolysis for months. It can be easily seen from Fig. 2 that the results with water are highly anomalous in all the three respects. First, there is a strong deficit (about 60% for the total gas); neither

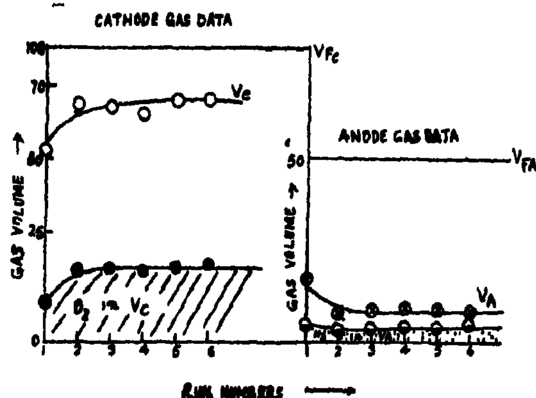


Fig. 2. Gas volumes in the cathode and anode compartments with the progress of electrolysis of water, -O-O- represents the volume of cathode gas and -⊗-⊗- that of anode gas. The striped area denotes the amount of oxygen in the cathode gas and the dotted area that of hydrogen in the anode gas

V_C nor V_A approaches anywhere near the theoretical value. Secondly, more oxygen goes to the cathode than hydrogen to the anode. As a result the observed ratio, V_C/V_A, is much higher than the theoretical value of 2. Thirdly and most unexpectedly, the cathode gas contains a liberal percentage of oxygen and the anode gas that of hydrogen, so much so, that the cathode gas as well as the anode gas violently explode on sparking. No co-liberation is, of course, observed in the coulometric gases which are practically Faradaic.

With the addition of gradually increasing amounts of sodium sulphate, the results continue to remain highly anomalous even for 10^{-4} N solution. The anomalies, however, gradually decrease as the electrolyte concentration is further increased gradually and at very high concentration like N Na_2SO_4, the results become almost Faradaic without showing any of the anomalies. Such gradual decrease in anomalies is shown in Fig. 3, current being kept constant at 1 mA/cm^2. It is evident from the above that the concentration of the electrolyte or ion population near the electrodes has a strong influence on the occurrence of anomalous electrolysis and the transition from non-Faradaic to Faradaic behaviour takes place around 10^{-1} N solution. It also depends upon the nature of the electrolyte besides current density and the former point will be discussed in a separate communication.

(ii) *Effect of increasing current density :* Experiments are carried out at various current densities while the concentration of the electrolyte is kept constant. With 10^{-3} N solution, we could not go much beyond about 10 mA with our available voltage and the results are still somewhat non-Faradaic as shown in Fig. 4. So the transition to Faradaic behaviour with increase in current density could not be observed for such low concentration with the facilities at our disposal. Neither could we see this transition conveniently with N solutions because they are practically Faradaic down to 1 mA or so. Decinormal solutions are also almost Faradaic and the non-Faradaic features are not prominent at all. So we chose 10^{-2} N solution for detailed study. These results corroborate our previous findings and are shown in Fig. 5. A small

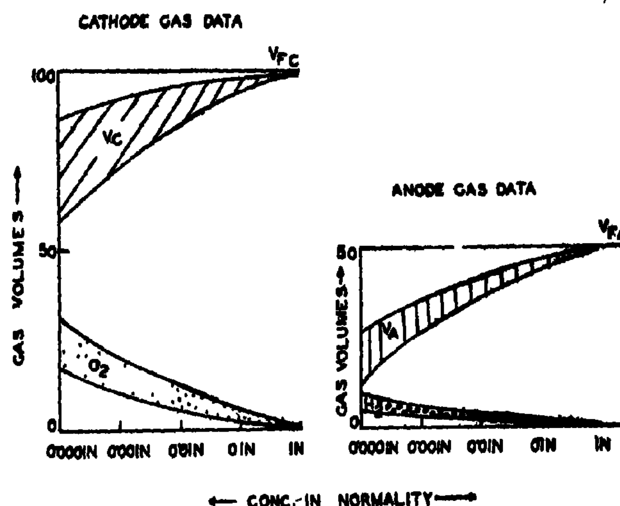


Fig 3 Results of electrolysis at 1 mA/cm² current density of sodium sulphate solution at different concentrations V_C and V_A represent the volumes of gases liberated at the cathode and anode respectively, the dotted area denotes the amount of oxygen in the cathode gas and the area filled with small circles the amount of hydrogen in the anode gas.

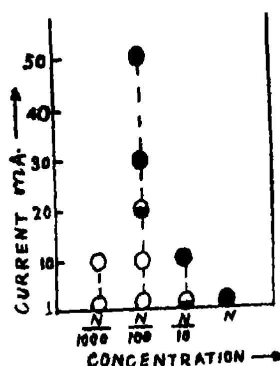


Fig 4 Results of electrolysis of a sodium sulphate solution at different current densities. O, ⊖ and ● denote respectively non-Faradaic, less non-Faradaic and completely Faradaic nature of electrolysis

amount of co-liberation remains even at 50 mA/cm². It is opportune here to mention a complicating factor viz., the programming of current as discussed below under (b).

(a) *Dependence on current density :* The foil electrodes show more prominent non-Faradaic features than the wire electrodes presumably due to much more variation of current density in the former. To cite an example, a 10^{-3} *N* Na_2SO_4 solution on electrolysis with a wire electrode gives nearly Faradaic volumes of gases in both the cathode and anode compartments, and the contamination in any gas does not exceed 10% whereas during electrolysis of the same solution with foil electrode the deficits in the cathode and anode gas volumes are 10% and 20%, the two gases being contaminated to the extent of 19% and 22%, respectively. So, for the study of non-Faradaic electrolysis, we have consistently used the foil electrodes.

(b) *Dependence of the results on previous history :* While studying the effect of current density, we came across an unexpected complication, particularly with the borderline concentration of 10^{-3} *N*, such that the results depend on the history of electrolysis. This makes it difficult to locate exactly the transition zone from non-Faradaic to Faradaic with respect to current densities. The complicating factor is that if the electrolysis is conducted at, say, 20 mA to start with, the results are Faradaic. But if the solution is subjected to low current electrolysis over a long period and the current is gradually increased to about 20 mA, the non-Faradaic behaviour persists at least to some extent. This is observed particularly with 10^{-3} *N* solution which is the zone of transition between non-Faradaic and Faradaic. So 20 mA/cm² may be regarded as the current density where the non-Faradaic features disappear and the electrolysis becomes Faradaic provided there is no initial low current electrolysis. The cause of this behaviour is probably the fact reported by one of the authors[4] that low current electrolysis in U-tubes as also in W-tube produces structure formation of sharp static boundary.

Theory :

A number of theories have been suggested to explain the features of non-Faradaic electrolysis[1,2]. To name some, they are interelectrode diffusion, local action, voltage induced decomposition of water, space charge formation, electronic conduction, reverse charging of the liberated gases and their

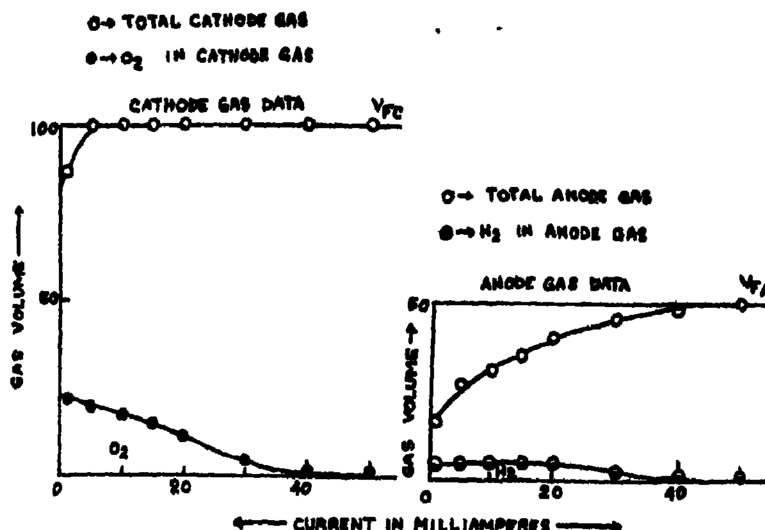


Fig 5 Effect of increasing the current density on the electrolysis of $10^{-2}N$ Na_2SO_4 solution.

subsequent migration, formation of charged water molecules $(H_2O)_x^+$ and probably $(H_2O)_x^-$ and their subsequent migration, and so on. Except the last two, the others are obviously incompatible with the observed facts.

Konya[5] has recently studied non-Faradaic electrolysis and has proposed that the anomalous results are due to the impurities present in the electrolyte solution and electrolysis of pre-electrolysed solution would lead to Faradaic results. But this idea does not conform to the fact repeatedly observed by us that co-liberation tends to increase with progress of electrolysis (Fig. 1). Secondly, if Konya's contention of local cell formation is accepted, this would lead to an excess rather than a deficit. Besides, to obtain consistent results, non-Faradaic electrolysis has to be studied by prolonged electrolysis liberating large volumes of gases after neglecting the first run whereas Konya, as also Gosnell and Venugopalan[6] have collected only one or two ml of gas presumably from the first run, which is certainly not the best way to study non-Faradaic electrolysis.

Though the theory of reverse charging of the liberated gases and their subsequent migration appears to be sufficient for explaining lower co-liberation at higher current density, it is unable to explain why cathodic preference is so common, very much more so if the cathode is a 'lilliput' electrode[7].

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Cyclocondensation and Cycloaddition Reactions on the Unsaturated Centre of Arylidene-2-aminobenzoxazole

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Arylidene-2-aminobenzoxazoles (III) were prepared by the condensation of 2-aminobenzoxazole with aromatic aldehydes. Cyclocondensation of mercaptoacetic acid, chloroacetyl chloride and diazoalkanes on III, give the corresponding 4-thiazolidinones (IV), azetidinones (V) and triazolines (VI) respectively. The biological activities of the prepared compounds were screened against some bacteria and fungi.

BENZOXAZOLE derivatives are reported to possess anti-inflamatory[1], antiseptic[2], food and feed preservation[3] and antimicrobial detergent[3,4] properties. It was of interest to incorporate benzoxazole molecule into the well known antimicrobial nuclei thiazolidinone, azetidinone and triazolines and to evaluate their biological activities. On this basis, synthesis and structural elucidation of some new benzoxazolothiazolidinones, benzoxazoloazetidinones and benzoxazolotriazolines were undertaken.

2-Aminobenzoxazole was reported[5] to be formed through direct interaction of hydroxylamine with benzoxazole in alkaline medium. However, when we tried its synthesis, a preliminary intermediate crystalline product, 2-hydroxylamino-2,3-dihydrobenzoxazole (I), was obtained. It was transformed into the corresponding 2-aminobenzoxazole (II) when boiled in 10% NaOH solution or on heating at 180-200° for 5 min.

The structure of the intermediate compound I was confirmed by its ir spectrum which showed two stretching vibration bands at 3300 cm^{-1} and 3150 cm^{-1} characteristic of NH—OH association, a band at 1250 cm^{-1} of C—N and a strong absorption band at 1100 cm^{-1} of C–O–C[6]. Its nmr spectrum was characterised by $\delta = 6.9$ (4 H, s, aromatic) and $\delta = 7.3$ (1 H, m, –CH).

Condensation of 2-aminobenzoxazole (II) with aromatic aldehydes in ethanol solution and piperidine gave the corresponding products, arylidene-2-aminobenzoxazoles (III).

The structure of compounds III has been established from their analytical data (cf. Table 1). The ir spectra showed absorption bands at 1640-1605, 1605-1590 and 1560-1545 cm^{-1} for the oxazole system[7] and band at 1670-1640 cm^{-1} for C=N group.

The interaction of mercaptoacetic acid with compounds IIIa, b, d, e, f and i in dry benzene produced cycloaddition products, 3-(2-benzoxazolyl)-4-thiazolidinones (IV) (cf. Table 1). In the ir spectra, the stretching vibration band characteristic of the >C=O group[8] was observed at 1700-1695 cm^{-1}.

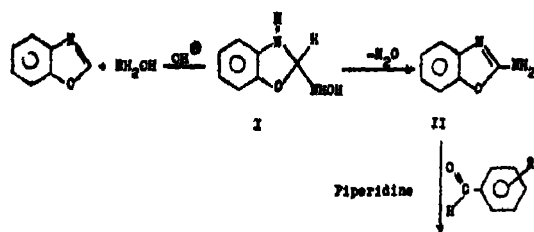
β-Lactam ring structure is known[9] to be the part of the molecules responsible for the antibiotic activity of penicillin and cephalosporine C. Cycloaddition of IIIa, b, e and g with monochloroketene (prepared *in situ* from chloroacetylchloride and triethylamine) in dry benzene gave rise to 1-(2-benzoxazolyl)-2-azetidinones (V). The ir spectra of compounds V showed stretching vibration bands characteristic of the >C=O group (of monocyclic β-lactam structure[6,10]), observed at 1705-1700 cm^{-1}.

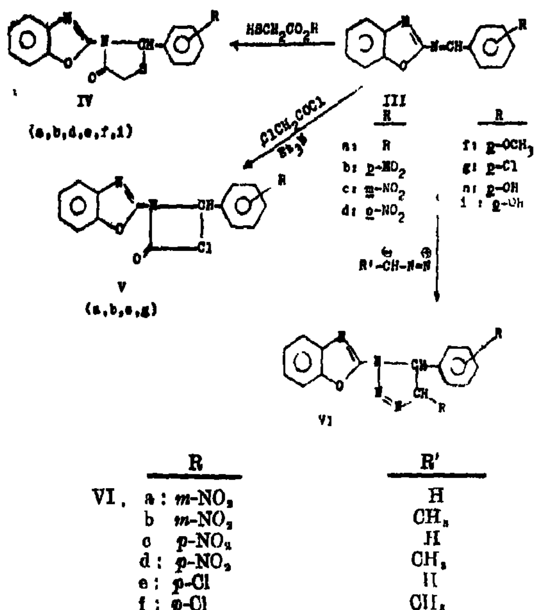
Diazoalkanes were recorded[11-13] to condense with Schiff bases to give the corresponding cycloaddition products.

Arylidene-2-aminobenzoxazoles (IIIa-g) were treated with diazoalkanes (methane, ethane, propane and butane) in dry ether at –5° for 15 days. The compounds IIIb, c and g reacted successfully with diazomethane and ethane producing the corresponding 1,2,3-triazolines (VI). However, the compounds IIIa, b, e and f were recovered unreacted from the reaction mixture. The ir spectra of VI showed stretching vibration band at 1660 cm^{-1} characteristic of -N=N- group and an absorption band at 1240-1245 cm^{-1} characteristic of C–N group[6].

Antibacterial and antifungal activities: Compounds of type III, IV and VI were tested *in vitro* for their biological activities on a variety of Gram-positive and Gram-negative bacteria[14] such as *S. aureus*, *P. pyocyanea*, *Proteus*, *E. coli* and *Serratia* and the fungi[15] *A. niger*, *A. flavus* and *P. notatum*.

The results showed that most of the prepared compounds III, IV, V and VI possessed from a little to strong activities against the tested bacteria and fungi. The activity ranging from 36 to 75% inhibition was found at a concentration $10^{-3}M$. The strongly active compounds against *S. aureus* were





IIIa, b, g and i; IVb, d, f and e), against *P. pyocyanea*, *Proteus* and *E. coli* were IIIb, g and i; IV b, e and f; Vb, e, g and VIe and f, against *Serratia* were IIIb, c; IVb and d; Vb and e and VIb and against *A. niger*, *A. flavus* and *P. notatum* were IIIa, d, g and i; IVb and e; Vb and g and VIc and d, respectively.

Experimental

Melting points reported are uncorrected. The ir spectra (KBr) were recorded on a Pye-Unicam SP 200 G spectrophotometer. The uv spectra in spec. pure ethanol were taken on a Pye-Unicam SP 8000 Ultraviolet spectrophotometer. Silica gel "chromatographic grade" was used for preparing chromatoplates. NMR spectra in trifluoroacetic acid were recorded on a Varian, 60 MHz.

2-Aminobenzoxazole[8] *and 2-hydroxylamino-2,3-dihydrobenzoxazole (I)*: A mixture of benzoxazole (3.54 g), hydroxylamine hydrochloride (2.1 g) and sodium hydroxide (45 ml; 1 *N*) was stirred for 3-4 hr on a water bath. The reaction mixture was cooled, whereby the crude 2-aminobenzoxazole was precipitated. This was filtered and recrystallized from benzene or water, m.p. 129-30°.

When the above procedure was carried out in lower concentration of NaOH (35 ml; 1 *N*), the precipitate recrystallized from benzene or water into compound I, m.p. 110° (mixed m.p. with 2-aminobenzoxazole 82°). It was easily soluble in cold dilute hydrochloric acid, slightly soluble in

TABLE 1—PHYSICAL DATA OF COMPOUNDS III, IV AND V

Compound* No.	R	m.p °C	Solvent of cryst.	Yield %	λ_{max} nm	ε value	IR ν cm⁻¹
III, a	H	175	Pet ether 70-100	60	290 335	2200 2000	1660 C=N
b	p-NO_2	267	Benzene	70	—	—	1642 C=N
c	m-NO_2	230	Benzene	57	—	—	1645 C=N
d	o-NO_2	174	Benzene Pet. ether	55	290 305	2400 1500	1645 C=N
e	p-$N(CH_3)_2$	230	Benzene	65	410 430	60000 64000	1668 C=N
f	p-OCH_3	135	Benzene Pet. ether	50	—	—	1663 C=N
g	p-Cl	182	Toluene	55	—	—	1658 C=N
h	p-OH	210	Toluene	58	—	—	1665 C=N
i	o-OH	185	Benzene	55	290 345	2300 9600	
IV, a	H	180	Benzene	40	—	—	1709 C=O
b	p-NO_2	100	Benzene	60	—	—	1695 C=O
d	o-NO_2	150	Benzene	50	—	—	1700 C=O
e	p-$N(CH_3)_2$	178	Benzene	55	—	—	1705 C=O
f	o-OH	160	Chloroform	45	—	—	1702 C=O
i	p-OCH_3	145	Chloroform	40	—	—	1700 C=O

(Table 1 Contd.)

V, a	H	210	Ethanol	32	—	—	1705 C=O
b	p-NO_2	190	Ethanol	35	—	—	1702 C=O
e	p-$N(CH_3)_2$	256	Benzene	45	—	—	1700 C=O
g	p-Cl	140	Ethanol	30	—	—	1702 C=O

* Satisfactory C, H, N and S analyses were obtained for all the compounds

TABLE 2—PHYSICAL DATA OF COMPOUNDS VI

Compound* No (VI)	R	R′	m p °C	Solvent of cryst	Yield %	(IR), νcm^{-1} N=N	C–N
a	m-NO_2	H	205	Dil acetic	58	1660	1245
b	m-NO_2	CH_3	293	Benzene	50	1658	1240
c	p-NO_2	N	150	Ethanol + pet ether	75	1660	1240
d	p-NO_2	CH_3	298	Ethanol + benzene	70	1658	1242
e	p-Cl	H	306	Benzene	50	1658	1240
f	p-Cl	CH_3	275	Benzene	52	1657	1240

* Satisfactory C, H and N analyses were obtained for all the compounds

cold NaOH solution and gave no violet colour with $FeCl_3$ (Found C, 55.10, H, 4.97; N, 18.30 Calcd.; C, 55.26; H, 5.26; N, 18.42%).

Effect of heat on 2-hydroxylamino-2,3-dihydrobenzoxazole (I): A dry sample of I (1 g) was heated on oil bath for 5 min at 180-200°, the melt was cooled to room temperature and crystallized from benzene, mixed m.p. with 2-aminobenzoxazole was unchanged (129-30°). The product showed the same ir spectrum and tlc analysis (R_f 0.81 benzene : n-hexane=3 : 1) as of 2-aminobenzoxazole.

Effect of 10% NaOH on 2-hydroxylamino-2,3-dihydrobenzoxazole (I) A mixture of I (1 g) and 10% sodium hydroxide solution (10 ml) was boiled for 10 min and cooled. The precipitate was filtered, dried and crystallized from benzene Its m.p. and mixed m.p. with 2-aminobenzoxazole was unchanged. It showed superimposable ir spectrum and identical tlc analysis with an authentic sample.

Arylidine-2-aminobenzoxazoles (III): Equimolecular amounts (0.01 mole) of the aldehyde and 2-aminobenzoxazole was refluxed in dry alcohol (15 ml) in presence of a few drops of piperidine for 3 hr. The reaction mixture was concentrated and cooled. The precipitate was filtered and recrystallized from proper solvent (Table 1).

Substituted 3-(2-benzoxazolyl)-4-thiazolidinones (IV): A mixture of Schiff base III a, b, e, f and i (0.02 mole) and of mercaptoacetic acid (0.02 mole) in 100 ml dry benzene was refluxed with a water separator until the theoretical amount of water had been collected. Excess benzene was evaporated, the residue washed with a 1 : 1 mixture of benzene-petroleum ether (40-60) several times, dissolved in ether and seeded. The product so obtained was recrystallized from proper solvent (Table 1).

Substituted 1-(2-benzoxazolyl)-2-azetidinones (V) To a mixture of Schiff bases III a, b, e and g (0.(mole) and NEt_3 (0.02 mole) in dry benzene (40 m was added monochloroacetyl chloride (0.02 mol dropwise at room temperature. The mixture w stirred for 5 hr and kept at room temperature for days. The precipitate formed (triethylami hydrochloride) was filtered, washed with the sa solvent. The combined solvent and the filtra was washed with dil. HCl and water and dried ov anhydrous $MgSO_4$. After filtration the solve was evaporated under reduced pressure. Th residue was collected and crystallized from prop solvent (Table 1).

1,2,3-Triazolines (VI) Ethereal solutions of th Schiff base III a, b, c, d, e, f and g (1 g) was treate with excess of cold ethereal diazoalkanes (diazome thane, diazoethane, diazopropane and/or diazo butane). The reaction mixture was kept at −5° fo 15 days, during which fresh amounts of ethere diazoalkane solution were added after 5 days. Th ether was then evaporated and in every case th product was filtered, washed with light petroleu ether (40-60) and crystallized from the prope solvent (Table 1). For the Schiff bases havin p-$N(CH_3)_2$, p-OCH_3 and o-nitro group in th arylidene moiety, the starting compounds wer recovered unchanged. For diazopropane an diazobutane no reaction took place with the Schif bases used. The results are listed in Table 2.

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Potential Antithyroid Agents. Part—V : Synthetic and Pharmacological Studies on Some N-aryl-N'-benzoylthiocarbamides

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The thiouréylene linkage exhibits certain desired effects required of an antithyroid drug. In search for some specific antithyroid agents, various N-aryl-N'-benzoylthiocarbamides have been synthesised by the condensation of benzoylisothiocyanate with different amines. Preliminary pharmacological investigations of some of the titled compounds showed promising results.

THE antithyroid agents are of great therapeutic interest as they offer a method for correcting a hyperfunctioning gland without resort to surgery. They lower the metabolic rate by interfering with synthesis, release or peripheral action of the thyroid hormone. The highly active antithyroid substances contain thiourea moieties, NHCSNH, capable of being oxidized easily, and suggestion has been made that the interference with thyroxine synthesis is by a direct reaction between I_2 and SH (formed by enolization) to form a disulphide[1-4]. As a part of general study directed towards the development of antithyroid agents[5-8], the above rationale led to a study of synthesis and biological evaluation of N-aryl-N'-benzoylthiocarbamides.

The present communication deals with the synthesis and pharmacological studies of some N-aryl-N'-benzoylthiocarbamides. The interest in the studies of these compounds as antithyroid drugs is due to the fact that acylisothiocyanates possess enhanced reactivity on account of the electron withdrawing acyl groups attached to the thioureido linkage and the acylisothiocyanates, on reaction with amino compounds, usually give acyl derivatives of thiocarbamides. The synthesis has been effected by the condensation of benzoylisothiocyanate with different amines.

Experimental

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. IR spectra were obtained using KBr pellets and a Perkin-Elmer 720 infracord spectrophotometer; bands reported were at least of medium intensity. The results of elemental analyses were in good agreement with those of theoretical values.

Benzoylisothiocyanate : It was prepared by the method reported in literature[9].

N-(p-Tolyl)-N'-benzoylthiocarbamide[10] *:* A warm solution of benzoylisothiocyanate (8.15 g ; 0.05 mole) in acetone (50 ml) was added dropwise with stirring to a solution of *p*-toluidine (5.35 g ; 0.05 mole) in acetone (50 ml) over a period of about 10 min. An exothermic reaction took place and the reaction mixture deposited a pale yellow crystalline product which was collected, washed with water and dried. It gave colourless shining needles from 70% ethanol, yield 13.58 g (97%) ; m.p. 157°. Anal. Found : N, 10.28 ; S, 11.74. Calcd. for $C_{15}H_{14}N_2OS$; N, 10.37 ; S, 11.85%.

Similarly, other N-aryl-N'-benzoylthiocarbamides were prepared by the condensation of benzoylisothiocyanate with different amines. The purification was achieved by several times recrystallisation with 70% ethanol (Table 1).

N-Aryl-N'-benzoylthiocarbamides have been characterised by elemental analyses ; ir spectra : 1510 (N=C=S), 1620 (C=N), 1300 (NH), 1680 (C=O) and 780 cm^{-1} (substituted benzene ring).

Pharmacological screening[11-13] *:* Male Sprague-Dawley rats (100-125 g) were maintained on a low-iodide diet for 3 days, then divided into groups of 4 rats each. Each animal in all the groups received an intraperitoneal injection of 1 ml of physiological saline, thiouracil, or one of the test compounds followed by, 1 μCu of $Na^{131}I$ after 1 hr. The animals were sacrificed and the thyroids removed. The whole lobes were placed in ground glass homogenizing tubes and counted in a Nuclear-Chicago well scintillation counter to determine total thyroid uptake. The whole lobes were then homogenized in 1 ml of 0.05 *M* barbital buffer (*p*H 8.6) containing 1.0×10^{-4} *M* thiouracil. 1 ml of cold 20% trichloroacetic acid (TCA) was added and the homogenate was centrifuged. The precipitate was washed twice with 1.0 ml of cold 10% TCA. The original supernatant liquid and the two washings were combined and the radioactivity determined. The ^{131}I in this fraction indicated the concentration of inorganic ^{131}I or TCA soluble ^{131}I. The washed precipitate was counted in the

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TABLE 1—N-ARYL-N'-BENZOYLTHIOCARBAMIDES

No.	R	Yield, %	Melting point °C
1.	H	90	140
2.	2-CH_3	95	117
3.	3-CH_3	85	121
4.	4-CH_3*	97	157
5.	2-OCH_3	88	123
6.	3-OCH_3	84	107
7.	4-OCH_3*	86	147
8.	2-Cl*	91	120
9.	3-Cl	85	125
10.	4-Cl	90	136
11.	2-OC_2H_5	86	119
12.	4-OC_2H_5	92	152
13.	4-Br	82	160
14.	2,3-$(CH_3)_2$	85	150
15.	2,4-$(CH_3)_2$	89	98
16.	2,5-$(CH_3)_2$	87	127
17.	2,4-$(OCH_3)_2$	80	142
18	2,5-$(OCH_3)_2$	86	138
19.	2,5-$(OC_2H_5)_2$	81	152
20.	2,3-Cl_2	78	156
21.	2,4-Cl_2	76	147
22.	2,5-Cl_2	79	150

* Known compounds

All the compounds gave consistent N and S analyses

TABLE 2—PHARMACOLOGICAL SCREENING RESULTS OF N-ARYL-N'-BENZOYLTHIOCARBAMIDES AS ANTITHYROID AGENTS IN INTACT RATS

Compounds	Thyroid radioactivity, dpm ± std error			Approximate estimated activity (thiouracil = 1.0)
	^{131}I uptake	$PB^{131}I$	Inorganic ^{131}I	
Blank	6478±50	7196±14	1238±28	
Thiouracil	4463±62	3822±30	620±18	1.0
1.	5342±25	4698±15	624±12	<1
2.	5484±18	4837±13	609±16	<1
3.	5650±16	5112±14	510±20	<1
4.	5722±14	5121±13	581±16	<1
5.	4920±17	4226±14	658±25	<1
6.	4822±13	4014±16	648±17	<1
7.	4882±15	4160±18	647±12	<1
8.	4626±12	4025±16	542±18	<1
9.	4768±16	4176±10	567±13	<1
10.	4294±18	3712±17	530±15	>1
11.	5468±14	4718±12	678±16	<1
12.	5371±20	4781±22	559±13	<1
13	5016±12	4528±20	448±17	<1
14.	5520±18	4892±20	582±14	<1
15	5730±15	5124±12	572±13	<1
16	5650±18	5127±18	508±16	<1
17	5621±12	4973±20	613±14	<1
18.	4632±22	4008±13	608±14	<1
19	4649±15	4124±12	508±12	<1
20	4038±22	3489±12	526±14	⩾1
21	4175±19	3562±18	582±18	⩾1
22.	4382±24	3698±15	675±11	⩾1

homogenizing tube. The radioactivity in this fraction indicated the $PB^{131}I$ (protein-bound-iodine) or the TCA precipitable ^{131}I. The counts were all corrected for counting efficiency and expressed as disintegration per minute.

All the compounds were dissolved in physiological saline for injection Thiouracil was dissolved with heating to 55°. Some of the compounds were injected as a suspension in saline. All compounds were assayed at concentrations equimolar to thiouracil. Table 2 summarizes the results of screening of these compounds.

All compounds possess antithyroid activity to some extent and appear to inhibit incorporation of I_2 in a manner similar to thiouracil. Compounds No. 10, 20, 21 and 22 appear to be slightly more potent than thiouracil.

Mode of action and effect of substituents on antithyroid activity : The thioureylene linkage in these compounds is capable of forming an-SH grouping by enolisation. The suggestion has been made that the interference with thyroxine synthesis was by a direct reaction between iodine and sulphydryl groupings to form a disulphide[16]. Since this reaction proceeds at a rate considerably faster than the iodination of tyrosil group, the competition could be quite favourable for diversion of iodine away from organic binding.

These data suggest that a disulphide bond in thyroid tissue is cleaved by antithyroid compounds containing a thioureylene linkage to form a new disulphide bond. This formulation is supported by chemical studies in which thiourea was found to cleave the disulphide bond of cystine to yield the mixed disulphide s-guanylthio-l-cysteine[17].

It is evident from the results of pharmacological studies that the introduction of chloro group in a benzene ring enhances the activity upto some extent.

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Synthesis and Pharmacology of 2-Aryl-5-Aryloxyalkyl-s-Triazolo[3,4-b]-1,3,4-Thiadiazoles

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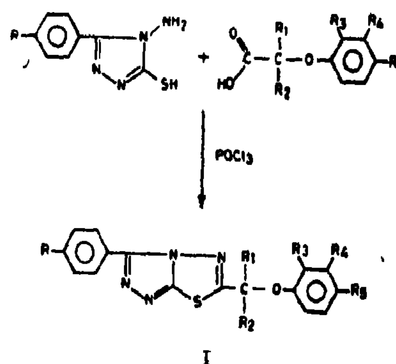
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A number of new s-triazolo[3,4-b]-1,3,4-thiadiazoles carrying aryl moiety at 2 position and aryloxyalkyl group at 5 position were synthesised and evaluated for their pharmacological activity. Some compounds exhibited strong CNS depressant, mild hypocholesterolemic and hypotensive action in experimental animals.

S-TRIAZOLES[1-6] and 1,3,4-thiadiazoles[7-9] are reported to exhibit broad spectrum of biological and pesticidal activities. It is observed[10] that s-triazoles fused to 1,3,4-thiadiazoles have not been explored for their biological activity. Our earlier work on the synthesis of 2-aryl-5-aryl/aralkyl-s-triazolo[3,4-b]-1,3,4-thiadiazoles[11] revealed CNS depressant and mild to strong antiinflammatory activity for the compounds.

Incorporation of appropriate aryloxyalkyl moiety in the heterocyclic residues[12,13] such as pyrroles, pyrazoles and oxadiazoles has led to the compounds possessing CNS depressant, antiinflammatory, hypocholesterolemic and hypotensive action. These findings prompted us to synthesise 2-aryl-5-aryloxyalkyl-s-triazolo[3,4-b]-1,3,4-thiadiazoles represented by structure I with a view to explore the possibility of obtaining biologically useful compounds.

The synthesis of I was accomplished in one step by reacting 3-aryl-4-amino-5-mercapto-1,2,4-triazoles with aryloxyalkyl carboxylic acids in presence of phosphorusoxychloride. The title compounds along with their pharmacological data are described in Table 1.



R = H or Cl, R_1 and R_2 = H or CH_3
R_3 = H, CH_3 or Cl R_4 = H or CH_3, R_5 = H or Cl.

TABLE 1—2-ARYL-5-ARYLOXYALKYL-s-TRIAZOLO[3, 4-b]-1,3, 4-THIADIAZOLES

Sl No	R	R_1	R_2	R_3	R_4	R_5	m p °C	% Decrease in motor activity at 100 mg/kg (i p mice)	Hypotensive action at 5 mg/kg mm
1	H	H	H	H	H	H	153-5	67	-18
2	H	CH_3	H	H	H	H	136-8	60	-33
3	H	H	H	H	H	Cl	172-4	23	–
4.	H	CH_3	H	H	H	Cl	158-60	38	-28
5.	Cl	H	H	H	H	H	183-4	38	-14
6.	Cl	CH_3	H	H	H	H	145-7	58	–
7	Cl	H	H	H	H	Cl	185-7	32	–
8	Cl	CH_3	H	H	H	Cl	198-9	35	–
9	H	CH_3	CH_3	H	H	H	207-9	34	-27
10.	H	CH_3	CH_3	H	H	Cl	153-4	46	-19
11	H	CH_3	CH_3	CH_3	H	Cl	170-1	35	-16
12.	H	CH_3	CH_3	H	CH_3	Cl	172-4	40	-38
13.	H	CH_3	CH_3	Cl	H	Cl	171-3	45	-50
14	Cl	CH_3	CH_3	H	H	H	176-8	59	-30
15	Cl	CH_3	CH_3	H	H	Cl	170-2	55	-30
16.	Cl	CH_3	CH_3	CH_3	H	Cl	171-2	42	-28
17.	Cl	CH_3	CH_3	H	CH_3	Cl	166-8	65	-29
18	Cl	CH_3	CH_3	Cl	H	Cl	200-3	36	-33

Elemental analysis (C, H, N) were within ±0.5% of the theoretical values.

Experimental

All the melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 221 infrared spectrophotometer and pmr spectra were taken on a Varian A60A spectrometer using TMS as the external standard. Mass spectra were recorded at 70eV on a Hitachi RMU 6L Mass spectrometer. All compounds were checked for their purity on tlc plates and characterised by elemental analysis and spectral studies. 3-Aryl-4-amino-5-mercapto-1,2,4-triazoles were prepared by the method of Heindel[14].

2-Phenyl-5-phenoxymethyl-s-triazolo[3,4-b]-1,3,4-thiadiazole (1) : A mixture of 3-phenyl-4-amino-5-mercapto-1,2,4-triazole (3.84 g ; 0.02 mole), phenoxyacetic acid (3.04 g ; 0.02 mole) and $POCl_3$ (20 ml) was heated under reflux for 4 hr. The excess $POCl_3$ was removed and the mixture was poured over crushed ice. The reaction mixture was made alkaline with 10% sodium bicarbonate. The product was filtered, washed with water and recrystallised from ethanol. ν_{max}^{KBr} 1590 (aromatic C=C), 1640 (C=N) and 1240 cm^{-1} (ether linkage). M^+ at m/e 308.

Compounds 2-9 were synthesised in similar manner.

2-Phenyl-5-[α-(4-chlorophenoxy)isopropyl]-s-triazolo[3,4-b]-1,3,4-thiadiazole (10) : 3-Phenyl-4-amino-5-mercapto-1,2,4-triazole (3.84 g ; 0 02 mole), α-(4-chlorophenoxy)isobutyric acid[15] (4.29 g , 0 02 mole) and $POCl_3$ (20 ml) were mixed and refluxed for 5 hr. The cooled reaction mixture, after removal of excess $POCl_3$, was poured into ice water, made alkaline by adding sodium bicarbonate solution and the resulting solid was filtered. It was recrystallised from ethanol to give the title compound. PMR ($CDCl_3$) δ1.81 (s, 6H, isopropyl protons) and 7.03-7.85 (m, 9H, aromatic protons). M^+ at m/e 370.

Compounds 11-18 were prepared in the same way.

Pharmacological evaluation : The compounds listed in Table 1 were subjected to primary screening in experimental animals at the Department of Pharmacology, G. S. Medical College, Bombay. Toxicity (LD_{50}), antiinflammatory, hypotensive, hypocholesterolemic and motor activities were determined by literature methods[16-18]. All the compounds were devoid of toxicity (LD_{50}>800 mg/kg oral p.o.). They did not exhibit promising antiinflammatory activity in comparison to phenylbutazone. Compounds 10-13 and 15-18 were screened for the hypocholesterolemic activity employing clofibrate as the control standard. Compounds 11 and 15 exhibited mild hypocholesterolemic activity. Compounds 1, 2 and 17 exhibited significant CNS depressant activity while compounds 2, 12, 13 and 18 showed appreciable hypotensive activity.

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Thiazolidinones as Potential Antibacterial Compound. Part—I

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2-Aryl-3-(3-uridophenyl)-4-thiazolidinones (II) have been prepared from the reaction of thioglycolic acid with azomethines in dry benzene. The azomethines have been prepared by condensation of different aromatic aldehyde with *m*-urido aniline. The compounds (II) show good antibacterial activity when tested against *S. aureus* and *E. coli* by nutrient agar pour plate method.

THIAZOLIDINONES have been found to exhibit antitubercular activity[1]. The nucleus is also active as hypnotic[2], anaesthetic[3] and antifungal[4]. Phenyl urea derivatives show central myorelaxant effect[5], motor incordinating activity, anticorazol[6] and anticonvulsive[7-10] activites.

For preparation of 4-thiazolidinones[11] of the type (II), the Schiff's[12] bases of 3-aminophenyl urea have been prepared with different aromatic aldehyde and condensed with thioglycolic acid in dry benzene. When tested, these compounds (II) showed antibacterial activity by disk diffusion method.

IR spectra of the title compounds were taken on a Beckmann spectrophotometer. The strong bands at 1750 cm^{-1}, 1760 cm^{-1} were characteristic carbonyl stretching frequency for thiazolidinone ring system.

Experimental

To the solution of aldehyde (0.01 *M*) in ethanol (50 ml; 95%) was added *m*-urido aniline (0.01 *M*) in ethanol (50 ml; 95%). The contents were heated to reflux for 2 hr, cooled and worked out to get the corresponding Schiff's base: $-C_6H_4$ 115°; $-2-OH-C_6H_4$ 208°; $-2-OH-5-Br.C_6H_3$ 222°; $2-OH-3,5-diBr.C_6H_2$ 202°; $4-OCH_3.C_6H_4$ 160°; $4-N-(CH_3)_2.C_6H_4$ 110°; $CH-CH.C_6H_5$ 105°; $-3-OH.C_6H_4$ 165°; $-3.Cl.C_6H_4$ 115°; $-4.Cl.C_6H_4$ 150°; $-3NO_2$ 152°; $-4-NO_2$ 163°; $4-OH-3-OCH_3.C_6H_3$ 158°; $-4-OH-C_6H_4$ 180°.

Azomethine (0.01 *M*), dry benzene (100 ml) and thioglycolic acid (0.012 *M*) were heated to reflux (~ 25 hr), using a Dean and Stark water separator. The solvent was removed and the residue was treated with $NaHCO_3$ solution and filtered. The thiazolidinones were crystallised from ethanol (95%), (yield: 45%): $-C_6H_5$ 285°; $-2.OH.C_6H_4$ 301°; $-2.OH.5\ Br-C_6H_3$ 280°; $-2.OH\ 3,5$-diBr C_6H_2 248°; $-4.OCH_3.C_6H_4$ 245°; $4-N-(CH_3)_2\ C_6H_4$ 130°; $-CH=CH.C_6H_5$ 255°; $-3OH.C_6H_4$ 260°; $-3.Cl.C_6H_4$ 100°; $4.Cl.C_6H_4$ 280°; $-3NO_2.C_6H_4$ 238°; $-4NO_2.C_6H_4$ 216°; $-4.OH.3-OCH_3-C_6H_3$ 190°; $-4-OH.C_6H_4$ 278°.

Antibacterial activity: The compounds (II) were tested for antibacterial activities by nutrient agar pour plate method in dimethyl formamide and were found active against *E.coli* and *S.aureus* in various concentration.

Acknowledgement

The authors thank Bhavnagar University for a Research Scholarship to one of them (N. C. D.) and Dr. S. B. Trivedi, Director, Tuberculosis Research Centre, Amargadh for preliminary antibacterial testing.

TABLE 1—ANTIBACTERIAL ACTIVITY OF THE THIAZOLIDINONE OF THE TYPE

(II)

Sl No	R	*S. aureus*	*E. coli*
1	$-C_6H_5$	+	–
2.	$-2-OH-C_6H_4$	++	++
3	$2-OH.5-Br-C_6H_3$	++	+
4.	$2-OH-3,5-di-Br.C_6H_2$	++	++
5.	$4-OCH_3-C_6H_4$	+	–
6	$4-N-(CH_3)_2C_6H_4$	–	–
7	$CH=CH-C_6H_5$	–	–
8	$3-OH-C_6H_4$	+	–
9.	$3-Cl-C_6H_4$	+	–
10.	$4-Cl-C_6H_4$	+	+
11.	$3-NO_2-C_6H_4$	+	+
12.	$4-NO_2-C_6H_4$	+	+
13.	$4-OH-3-OCH_3-C_6H_3$	+	+
14.	$4-OH.C_6H_4$	+	+

All the compounds gave satisfactory C, H, N and S analyses.

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Local Anaesthetics. Part—II[1] : Synthesis of 2-(N,N-Disubstituted Aminoacetamido)-4-*p*-Fluorophenyl and -*m*-Methoxyphenyl Thiazoles

P. N. BHARGAVA, RAM LAKHAN* and RAMACHARYA TRIPATHI**

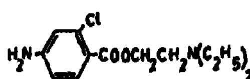
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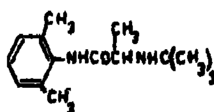
Thirteen new 2-(N,N-disubstituted aminoacetamido)-4-p-fluorophenyl and -m-methoxyphenyl thiazoles have been synthesised. Hydrochlorides of these compounds have been screened for their local anaesthetic activity by Frog's sciatic plexus method and the activity compared with that of procaine hydrochloride. Of these, 2-piperidinoacetamido-4-p-fluorophenylthiazole·HCl is the most potent; nearly 15 times in terms of onset of anaesthesia in comparison with procaine-HCl.

MARKS and Rubin[2] have claimed that chloroprocaine (1), (β-diethylaminoethyl 4-amino-2-chlorobenzoate) exhibits local anaesthetic activity comparable to that of procaine. Moreover, chloroprocaine is systemically less toxic due to its fast metabolic hydrolysis[3].

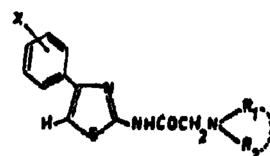
It has also been observed that the duration of anaesthesia and topical anaesthetic properties of procaine-like compounds are favoured by an increase of the aminoalkyl group and the intermediate alkylene chain. Thus, the dibutyl homologue butacaine, 3-dibutylaminopropyl 4-aminobenzoate[4], in which both the size of the N-alkyl groups and chain length are enlarged, is found to be nearly as active topically as cocaine[5]. Recently Takman *et al*[6] have reported that 2-(*t*-butylamino)-2',6'-propionoxylidide (2), a lidocaine homologue, has significantly long lasting local anaesthetic activity and sufficiently low acute toxicity.



(1)



(2)



(3)

where X = p – F or m – CH_3O.

Taking these facts into consideration and that the 2-aminothiazole derivatives[7,8] exhibit marked local anaesthetic activity, the authors have synthesised a series of fluorine and methoxy substituted 4-phenyl-2-(N,N-disubstituted aminoacetamido)thiazoles having the general formula (3).

2-Amino-4-*p*-fluorophenyl- and 2-amino-4-*m*-methoxyphenylthiazoles were prepared by the condensation of *p*-fluoroacetophenone or *m*-methoxyacetophenone with thiourea and iodine following a slightly modified method of Joshi and Bahel[9]. The 2-amino-4-arylthiazoles were treated with chloroacetyl chloride in dry benzene to give the corresponding 2-chloroacetamido-4-arylthiazoles. Reaction of these compounds with different secondary amines in absolute ethanol yielded 2-(N,N-disubstituted aminoacetamido)-4-arylthiazoles (Table 1). The hydrochlorides of these bases were prepared by usual methods (Table 2) and evaluated for conduction anaesthesia on frogs by the sciatic plexus method[10].

Experimental

All melting points were observed with a Gallenkamp apparatus and are uncorrected. Elemental analyses (C, H and N) were carried out on a Coleman analyser. The ir spectra were recorded on a Perkin-Elmer 720 grating spectrophotometer as nujol mulls and nmr on a Varian-A60D spectrometer at the probe temperature (44.5°) as CCl_4 or $CDCl_3$ solutions using TMS as an internal standard. The purity of compounds was checked by tlc using silica gel G (E. Merck).

*2-Amino-4-*p*-fluorophenylthiazole :* It was prepared from *p*-fluoroacetophenone by a slightly modified procedure of Joshi and Bahel[9]. The unreacted iodine was removed by washing with aqueous sodium thiosulphate and the product crystallised (EtOH), m.p. 120° (lit[9]. m.p. 120°).

*2-Amino-4-*m*-methoxyphenylthiazole :* It was prepared as above in 68% yield by reaction of *m*-methoxy-

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acetophenone, thiourea and iodine and crystallised from ethanol, m.p. 127° (Found : N, 13.8 ; S, 15.8. $C_{10}H_{10}N_2OS$ requires N, 13.6 ; S, 15.5%).

2-Chloroacetamido-4-p-fluorophenylthiazole : To an ice-cooled solution of 2-amino-4-*p*-fluorophenylthiazole (9.5 g) in dry benzene (60 ml), chloroacetyl chloride (4 ml) dissolved in dry benzene (30 ml) was added slowly with vigorous shaking. The reaction mixture was refluxed on a water bath for 3 hr. Benzene was distilled off and the residue treated with 5% $NaHCO_3$ solution to remove unreacted chloroacetyl chloride. The product was washed with water and recrystallised from ethanol, yield 80%, m.p. 135° (Found : N, 10.5 ; Cl, 13.3. $C_{11}H_8ClFN_2OS$ requires N, 10.3 ; Cl, 13.1%). IR : 3220m, 1730s, 1510s, 1240s cm^{-1}.

Likewise, 2-chloroacetamido-4-*m*-methoxyphenylthiazole was prepared. It was csystallised from ethanol, yield 75%, m.p. 145° (Found : N, 9.8 ; Cl, 12.3. $C_{12}H_{11}ClN_2O_2S$ requires N, 9.9 ; Cl, 12.6%). IR : 3300m, 1680s, 1590s, 1260s cm^{-1}.

2-Piperidinoacetamido-4-p-fluorophenylthiazole : A mixture of 2-chloroacetamido-4-*p*-fluorophenylthiazole (2.0 g), piperidine (1.0 ml), absolute ethanol (40 ml) and anhydrous potassium carbonate (1.0 g) was heated under reflux on a water bath for 8 hr. The excess of amine and ethanol was removed by distillation and the residue was treated with 10% sodium bicarbonate solution to remove acid impurities. It was crystallised from absolute ethanol, yield 70%, m.p. 152° (Found : C, 60.3 ; H, 5.4 ; N, 13.3. $C_{16}H_{18}FN_3OS$ requires C, 60.2 ; H, 5.6 ; N, 13.2%). IR : 3200w (N-H stretch), 1710s (C=O stretch), 1580s, 1510m, 1300s, 1250m cm^{-1}. NMR ($CDCl_3$) δ 6.95 – 8.20 (m, 5H, aromatic protons), 3.21 (s, 2H, $-COCH_2-N\langle$), 2.33 – 2.75 (resonance signals for 2′ and 6′ protons of the piperidine ring), 1.15 – 2.0 (resonance signals for 3′, 4′ and 5′ protons of the piperidine ring), 9.80 (br, 1H, -N*H*-) ppm.

Similarly, other 2-(N,N-disubstituted aminoacetamido)-4-*p*-fluorophenyl- and -4-*m*-methoxyphenylthiazoles were prepared by the reaction of different acyclic and cyclic secondary amines with 2-chloroacetamido-4-*p*-fluorophenylthiazole and 2-chloroacetamido-4-*m*-methoxyphenylthiazole separately. These were crystallised from ethanol. Their characterization data are given in Table 1. The r and nmr spectral data of compounds No. 1, 5, 6 nd 12 were typical of the structures assigned to hem.

Hydrochloride of 2-piperidinoacetamido-4-p-fluorophenylthiazole : A solution of 2-piperidinoacetamido-4-*p*-fluorophenylthiazole (2.0 g) prepared in nhydrous benzene was saturated with dry hydroloric acid gas. A solid mass was formed which as filtered and washed with dry ether. The crude oduct was crystallised from absolute ethanol, eld 80%, m.p. 252° (Found : C, 54.2 ; H, 5.2 ; , 12.2 ; Cl, 9.7. $C_{16}H_{19}ClFN_3OS$ requires C, .0 ; H, 5.4 ; N, 11.8 ; Cl, 10.0%).

TABLE 1—CHARACTERIZATION DATA OF 2-(N,N-DISUBSTITUTED AMINOACETAMIDO)-4-ARYLTHIAZOLES (3)

Sl. No	R_1	R_2	Yield %	m.p. °C	Formula
			X = *p*-F		
1.	Et	Et	65	110	$C_{15}H_{18}FN_3OS$
2.	Pr	Pr	70	259	$C_{17}H_{22}FN_3OS$
3.	*i*-Pr	*i*-Pr	72	273	$C_{17}H_{22}FN_3OS$
4	*n*-Bu	*n*-Bu	65	233	$C_{19}H_{26}FN_3OS$
5.	*i*-Bu	*i*-Bu	80	141	$C_{19}H_{26}FN_3OS$
6.	$C_6H_5CH_2$	$C_6H_5CH_2$	80	115	$C_{25}H_{22}FN_3OS$
7.	$C_6H_5CH_2$	C_6H_5	75	182	$C_{24}H_{20}FN_3OS$
8	Piperidino		70	152	$C_{16}H_{18}FN_3OS$
9	Pyrrolidino		70	103	$C_{15}H_{16}FN_3OS$
			X = *m*-CH_3O		
10.	*i*-Bu	*i*-Bu	70	156	$C_{20}H_{29}N_3O_2S$
11	$C_6H_5CH_2$	$C_6H_5CH_2$	72	116	$C_{26}H_{25}N_3O_2S$
12.	Piperidino		75	112	$C_{17}H_{21}N_3O_2S$
18.	Pyrrolidino		65	118	$C_{16}H_{19}N_3O_2S$

Satisfactory C, H and N analyses were obtained

Following the above procedure, hydrochlorides of other 2-(N,N-disubstituted aminoacetamido)-4-*p*-fluorophenyl- and -4-*m*-methoxyphenylthiazoles were prepared. Their yields and melting points are recorded in Table 2. Satisfactory N and Cl analyses of the hydrochlorides were obtained.

Pharmacological screening for plexus anaesthesia on frogs : The base hydrochlorides reported in Table 2 were screened for their local anasethetic activity on frogs at 0.1% concentration of the compounds in 0.7% saline adopting the procedure of Bulbring and Wajda[10]. Three frogs were tested for each of the compounds and the average time of onset of anaesthesia was recorded. The results (Table 2) are compared with that of procaine hydrochloride used as the standard.

TABLE 2—LOCAL ANAESTHETIC ACTIVITY OF 2-(N,N-DISUBSTITUTED AMINOACETAMIDO)-4-ARYLTHIAZOLE HYDROCHLORIDES

Sl No	R_1	R_2	Yield %	m.p °C	Onset of anaesthesia (in minutes)*	
					0 05*N*	0.1*N*
			X = *p*-F			
1	Et	Et	60	142	0.50	0 55
2.	Pr	Pr	68	256	2.20	2.45
3	*i*-Pr	*i*-Pr	70	162	1.55	2.30
4.	*n*-Bu	*n*-Bu	72	131	1.10	1.20
5.	*i*-Bu	*i*-Bu	75	135	1.05	1.10
6	$C_6H_5CH_2$	$C_6H_5CH_2$	72	173	0 40	0.45
7	$C_6H_5CH_2$	C_6H_5	70	166	0.45	0.50
8	Piperidino		80	252	0.30	0.35
9.	Pyrrolidino		60	156	0 35	0.40
			X = *m*-CH_3O			
10.	*i*-Bu	*i*-Bu	65	140	10.00	11.00
11.	$C_6H_5CH_2$	$C_6H_5CH_2$	75	165	9 15	10.30
12.	Piperidino		75	260	6.10	6.45
18	Pyrrolidino		60	175	7.00	8.15
	Procaine Hydrochloride †				8.25	9.45

* Onset of anaesthesia in minutes after administration of anaesthetic, detected by using HCl of given normality ;

† Procaine hydrochloride (at 0.1% concentration) was used as such, as the standard.

Results and Discussion

From the screening results it is concluded that all the hydrochlorides of 2-(N,N-disubstituted amino-acetamido)-4-*p*-fluorophenylthiazoles are considerably more effective in producing onset of anaesthesia in frogs in comparison to procaine hydrochloride. Of these, 2-piperidinoacetamido-4-*p*-fluorophenylthiazole is the most potent local anaesthetic. The activity of different groups in hydrophilic moiety lies in the order : piperidino> pyrrolidino> benzyl> ethyl> isobutyl> *n*-butyl> isopropyl> *n*-propyl. But the hydrochlorides of 2-(N,N-disubstituted amino-acetamido)-4-*m*-methoxyphenylthiazoles require more or less the same time for the onset of anaesthesia as the standard.

It is also apparent that significantly quick response of the compounds No. 1-9 (in Table 2) to produce onset of anaesthesia is due to the presence of 4-*p*-fluorophenyl substituent. It is also interesting to note that 4-*p*-fluorophenylthiazole derivatives reported here are much more potent local anaesthetics than the substituted benzothiazole derivatives described in an earlier communication[1].

Acknowledgement

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Synthesis of 5-Aryl/Aryloxyalkyl-1,3,4-Oxadiazole-2-Thiones and Related Compounds as Possible Fungicides

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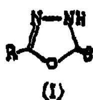
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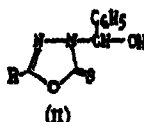
Eight 5-aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thione (I), eleven 3-hydroxybenzyl-5-aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thione (II) and twenty N,N'-*bis*-(3-methyleno/ethyleno-5-aryloxyalkyl-1,3,4-oxadiazole-2-thione)-phenylenediamines benzidines (III) have been prepared to study their antifungal activity. Most of them have been screened against two pathogenic fungi, *A. flavus* and *H. orysae* and found to be fungicidal.

THE oxadiazole ring is well known for its biological activities. Some 3-alkyl/phenyl carbamates of substituted-1,3,4-oxadiazole-2-thiones are reported as bactericides[1]. Several benzidine derivatives are also found to possess antimicrobial[2] and fungicidal[3] activities. Keeping these in view the title compounds have been prepared.

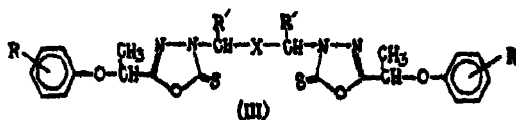
5-Aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thiones (I) were prepared by the reaction of aryl/aryloxyacyl hydrazines[4] with carbondisulfide in the presence of alkali[5]. I were condensed with benzaldehyde to give corresponding 3-hydroxybenzyl-5-substituted-1,3,4-oxadiazole-2-thiones (II). Reaction of I with aldehydes in the presence of phenylenediamine/benzidine gave corresponding N,N'-*bis*-(3,5-disubstituted-1,3,4-oxadiazole-2-thione)-phenylenediamines/benzidines respectively. The compounds were characterised by their elemental analyses and ir spectra.



(I)



(II)



(III)

Experimental

All the melting points are uncorrected. IR pectra were recorded in KBr.

5-Aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thiones[5] *(I)* : 'o an ethanolic (95%, 200 ml) solution of aryl/ryloxyacylhydrazine[4] (0.05 *M*), KOH (0.05 *M*), nd carbondisulfide (1 *M*) were added and the ·sulting solution was refluxed for 6 hr. It was ›ncentrated to a small volume, poured into iceater and filtered. The filtrate on acidification gave a precipitate which was filtered, washed and recrystallised from aqueous ethanol. The properties and analysis of oxadiazole-2-thiones are recorded in Table 1.

3-Hydroxybenzyl-5-aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thiones (II) : 5-Aryl/aryloxyalkyl-1,3,4-oxadiazole-2-thione (I), disssolved in ethanol (0.01 *M*), was cooled in an ice-bath. Benzaldehyde (0.01 *M*) was added to this. The mixture was kept in an ice-bath for 3 hr. The solid separating out was filtered, washed with cold ethanol and recrystallised. The properties and analysis of II are given in Table 2.

N,N'-Bis-*(3-methyleno/ethyleno-5-aryloxyalkyl-1,3,4-oxadiazole-2-thione)-phenylenediamines/benzidines (III)* : 5-Aryloxyalkyl-1,3,4-oxadiazole-2-thione (I), dissolved in ethanol (0.01 *M*), was cooled in an ice-bath. To this, formaldehyde/acetaldehyde (0.01 *M*) was added. An ethanolic solution of phenylenediamine/benzidine (0.005 *M*) was now added to it dropwise with swirling. The mixture was kept in an ice-bath for 3 hr. The solid separating out was filtered, washed and recrystallised with aqueous ethanol. The properties and analysis of III are given in Table 3.

Fungicidal activity : The compounds were screened for their fungicidal activity against *A. flavus* and *H. oryzae* by agar plate technique[6,7].

In general, compounds screened are more active towards *A. flavus* than *H. oryzae*. Compounds of Table 3 are more fungicidal than the parent oxadiazoles. The presence of phenoxymoiety at position-5 of oxadiazole ring increases the antifungal activity. Introduction of hydroxybenzyl group at position-3 also slightly increases the activity. There is no significant effect towards the fungicidal activity by introduction of benzidine moiety in place of phenylenediamine. The best antifungal compounds of this series are 21, 29, 32 and 38 having 5-*p*-chlorophenoxy moiety in the oxadiazole ring. All these observations are based on their comparison

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TABLE 1— 5-ARYL/ARYLOXYALKYL-1,3,4-OXADIAZOLE-2-THIONES (I)

Sl. No.	R	m.p. °C	Yield %	N% Found (Calcd.)	S% Found (Calcd.)	Antifungal activity Conc. 1 : 100,000	
						A. flavus	*H. oryzae*
1.[a]	4-HO-C_6H_4	208	74 6	14.15 (14.43)	16 27 (16.49)	–	–
2.	3,5-$(NO_2)_2.C_6H_3$	300	72 8	–	11.76 (11.94)	21 6	18.5
3.	4-$NO_2.C_6H_4$-O-CH_2	180	74 5	–	12.44 (12.64)	28.4	15.7
4.	3,5-$(CH_3)_2$ C_6H_3 -O-CH_2	186	78.7	–	13.38 (13.56)	–	–
5.	2-$(CH_3)_2$CH-5-$CH_3.C_6H_3$-OCH_2	113	72.6	10.24 (10 60)	11.94 (12.12)	38.2	29.4
6.	2-ClC_6H_4-O-CH (CH_3)	90	68 0	–	12.28 (12 47)	–	–
7.[b]	4-ClC_6H_4-O-CH (CH_3)	114-15	62.8	–	12.26 (12 47)	39.5	31.2
8.	4-$CH_3C_6H_4$-O-CH (CH_3)	135-37	67.7	–	13.40 (13.56)	28.0	17.8

a. ν_{max} 825 (p-substituted benzene), 1070 (C=S), 1600 (C=N) cm^{-1}.

b. ν_{max} 750 (C-Cl), 880 (p-substituted benzene), 1080 (C=S), 1230 (=C-O-C), 1620 (C=N) cm^{-1}

TABLE 2— 3-HYDROXYBENZYL-5-ARYL/ARYLOXYALKYL-1,3,4-OXADIAZOLE-2-THIONES (II)

Sl. No.	R	m.p °C	Yield %	N% Found (Calcd)	S% Found (Calcd)	Antifungal activity Conc. 1 : 100,000	
						A. flavus	*H. oryzae*
9.	2-$CH_3.C_6H_4$	145	68 2	–	10.56 (10 74)	–	–
10.	3-$CH_3.C_6H_4$	132	65 5	–	10.52 (10 74)	–	–
11.	4-CH_3 C_6H_4	180	68 8	9 06 (9 39)	10 58 (10 74)	20 0	12.8
12.[c]	C_6H_5-O-CH_2	95	72 2	–	9 98 (10 19)	22.7	15.4
13.	2-$CH_3.C_6H_4$-O-CH_2	92	74.6	–	9 58 (9.75)	–	–
14.	3-$CH_3.C_6H_4$-O-CH_2	82	67.8	–	9 50 (9 75)	22.9	15.7
15.	4-$CH_3.C_6H_4$-O-CH_2	104	70 5	–	9 48 (9 75)	23.2	16.0
16.	2-Cl.C_6H_4-O-CH_2	118	75 0	–	9 30 (9.18)	–	–
17.	4-Cl.C_6H_4-O-CH_2	137	76.4	7 75 (8 03)	9 00 (9.18)	44.0	33.3
18.	2-CH_3-4-Cl.C_6H_3-O-CH_2	85	67 4	–	8.65 (8.82)	46.4	36.2
19.	2,4$(CH_3)_2$ C_6H_3-O-CH_2	150	66 8	–	9.21 (9 35)	–	–

c. ν_{max} 750 (monosubstituted benzene), 1075 (C=S), 1240 (=C-O-C), 1600 (C=N) cm^{-1}.

TABLE 3— N,N′-*Bis*-(3-METHYLENO/ETHYLENO-5-ARYLOXYALKYL-1,3,4-OXADIAZOLE-2-THIONE)-PHENYLENE-DIAMINES/BENZIDINES (III)

Sl. No.	R	R′	X	m p. °C	Yield %	Analysis % Found (Calcd.)	Antifungal activity Conc. 1 : 100,000	
							A. flavus	*H. oryzae*
20.	2-Cl	H	p-$C_6H_4(NH)_2$	118	68.1	S 9.66 (9.86)	48.4	36.0
21.[d]	4-Cl	H	p-$C_6H_4(NH)_2$	147	65.3	S 9.64 (9.86)	50.2	36.4
22.	4-CH_3	H	p-$C_6H_4(NH)_2$	139	59.2	S 10.36 (10.59) N 13.64 (13.90)	28.3	24.7
23.	2-Cl	H	m-$C_6H_4(NH)_2$	Decomp.	52.6	S 9.62 (9.86)	–	–

(Table 3 contd.)

24.	4-Cl	H	m-$C_6H_4(NH)_2$	Decomp.	48.8	S 9.64 (9.86)	47.1	86.2
25.	4-CH_3	H	m-$C_6H_4(NH)_2$	>250	46.8	S 10.88 (10.59)	–	–
26.	4-Cl	H	o-$C_6H_4(NH)_2$	87	71.2	S 9.66 (9.86)	45.8	84.4
27.	4-CH_3	H	o-$C_6H_4(NH)_2$	112	79.4	S 10.40 (10.59)	–	–
28.	2-Cl	H	p-C_6H_4-$C_6H_4(NH)_2$	141	45.4	S 8.68 (8.87)	–	–
29.	4-Cl	H	p-C_6H_4-$C_6H_4(NH)_2$	152	98.6	S 8.66 (8.87) N 11.87 (11.65)	50.8	85.6
30.	4-CH_3	H	p-C_6H_4-$C_6H_4(NH)_2$	51	81.1	S 9.22 (9.41)	29.0	25.0
31.	2-Cl	CH_3	p-$C_6H_4(NH)_2$	107	45.0	S 9.25 (9.45)	–	–
32.	4-Cl	CH_3	p-$C_6H_4(NH)_2$	129	44.7	S 9.22 (9.45)	51.0	86.2
33.	4-CH_3	CH_3	p-$C_6H_4(NH)_2$	122	48.0	S 9 96 (10 12) N 13.00 (13.29)	28.8 –	24.5 –
34.	2-Cl	CH_3	m-$C_6H_4(NH)_2$	Gum	62 0	–	–	–
35	4-Cl	CH_3	m-$C_6H_4(NH)_2$	108	53.4	S 9 27 (9 45)	47.7	86 4
36.	4-CH_3	CH_3	m-$C_6H_4(NH)_2$	Gum	48.6	–	–	
37.	2-Cl	CH_3	p-C_6H_4-$C_6H_4(NH)_2$	112	78.9	S 8 72 (8 53)	–	–
38.	4-Cl	CH_3	p-C_6H_4-$C_6H_4(NH)_2$	66	79.0	S 8 74 (8 53)	51 4	86 0
39.[e]	4-CH_3	CH_3	p-C_6H_4-$C_6H_4(NH)_2$	129	67.8	S 9 18 (9 04)	29 2	25.8
	Memcge						75.4	87.4
	Blitox 50 WP						85 5	60 7

d. ν_{max} 740 (C-Cl), 810 (p-substituted benzene), 1280 (=C-O-C-), 1650 (C=N), 3350 (NH) cm^{-1}

e. ν_{max} 810 (p-substituted benzene), 1225 (=C-O-C-), 1640 (C=N), 3300 (NH) cm^{-1}.

against two commercial fungicides Memcge and Blitox 50 WP.

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Studies on Synthesis and Anthelmintic Activity of N-(Substituted Phenoxy Acetamido) Phthalimides

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A series of N-(substituted phenoxy acetamido)phthalimides (1-21) have been synthesised and screened for their cestodicidal activity against *Hymenolepis nana* infection in rats. The compound 14 was found to be the most active compound of the series showing 50.6% clearance of infection at a dose of 250 mg/kg given for 3 days.

PHTHALIC acid derivatives have been recently reported to possess marked anthelmintic activity[1]. The broad spectrum of biological activity has been associated with phenoxy acetic acid nucleus[2]. Hence, it was thought that the molecules containing both the moieties would have a more pronounced biological activity. The present paper describes the synthesis and anthelmintic activity of N-(substituted phenoxy acetamido)phthalimide (1-21).

Reactions of substituted phenols with ethyl chloro acetate and hydrazine hydrate yielded substituted phenoxy acetyl hydrazines[3]. Condensation of phenoxy acetyl hydrazines with substituted phthalic anhydride gave N-(substituted phenoxy acetamido)-phthalimides (1-21).

Experimental

The structure of all the compounds were checked by ir (KBr) recorded on Perkin-Elmer 157 and 177 infracord spectrophotometers. NMR spectra were recorded on Varian A60-D and Perkin-Elmer R_{32} spectrophotometers using TMS as internal reference. The chemical shifts are given in δ values. The mass spectra of the compounds were taken on JEOL-JMS-D300 instrument. Melting points were taken in open capillary and are uncorrected.

Synthesis of substituted phenoxy acetyl hydrazines : The substituted phenoxy acetyl hydrazines were prepared according to the method of Conti[3].

Synthesis of N-(4-nitrophenoxy acetamido)phthalimide (1) : A mixture of *p*-nitrophenoxy acetyl hydrazine (2.1 g ; 0.01 mole) and phthalic anhydride (1.48 g ; 0.01 mole) was heated on a free flame for 15 min. A jelly like mass separated out on cooling, which was washed with water. The solid thus separated was recrystallised from ethanol, m.p. 178°, yield, 2.0 g (60%). IR ν max (KBr) cm^{-1} : 3300 (NH), 2900 (CH_2), 1680 (C=O), 1520, 1340 (NO_2), 1245 (C–O–C). NMR ($CDCl_3$) : 8.0-8.5 (br,1, N*H*), 6.7-7.34 (m, 4, Ar-*H*), 7.5-7.9 (m, 4, phthalimide-Ar-*H*), 3.83 (s, 2, CH_2). Mass : M^+ at m/z : 341. Analysis : Found : C, 56.00 ; H, 2.94 ; N, 12.12. Calcd. for $C_{16}H_{11}N_3O_6$; C, 56.30 ; H, 3.22 ; N, 12.31%.

Other N-(substituted phenoxy acetamido)phthalimides (2-21) were prepared in a similar manner and the results are given in Table 1.

Biological activity : All the compounds were tested *in vivo* for their cestodicidal activity against *Hymenolepis nana* infection in rats by the technique of Steward[4]. The compounds were administered orally at dosages 500, 400 and 250 mg/kg using three rats per experimental group. Yomesan was used as the standard drug in all control experiments and it cleared 100% of the above infection at a single oral dose of 50 mg/kg. The results are summarised in Table 1.

TABLE 1

Sl. No.	R_1	R_2	m p °C	Yield* %	Cestodicidal activity against *H. nana* Dose mg/kg	% efficiency
			R=H			
1.	4-NO_2	H	178	60	250	12.2
2.	3-OCH_3	5-OCH_3	162	55	500	Inactive
3	4-CH_3	H	164	64	400	16.0
4.	2-CH_3	H	110	60	250	15.4
5	4-Cl	3-CH_3	204	70	250	20.0
6	4-C_6H_5	H	210	60	500	Inactive
7.	3-CH_3	H	112	60	400	18.2
8	2-CHO	H	262	65	400	18.0
9	2-Cl	H	148	70	250	22.4
10.	4-Cl	H	168	62	250	25.0
11.	H	H	120	67	250	28.0
			R=NO_2			
12.	4-C_6H_5	H	172	50	250	25.0
13.	4-Cl	3-CH_3	160	66	250	49.2
14.	4-NO_2	H	208	68	250	50.6
15.	4-CH_3	H	138	62	250	30.0
16.	3-CH_3	H	260	65	250	25.0
17.	2-Cl	H	184	59	250	45.8
18.	2-CHO	H	238	70	250	35.2
19.	2-CH_3	H	134	60	400	15.0
20.	H	H	154	60	250	23.0
21.	4-Cl	H	198	55	250	48.0

* All the compounds gave satisfactory C, H and N analyses and were within ±0.5% of the theoretical values.

Results and Discussion

The cestodicidal activity exhibited by N-(substituted phenoxy acetamido)phthalimides against *H. nana* infection in rats is shown in Table 1. The compound 14 at a dose of 250 mg/kg given for 3 days caused 50.6% removal of *H. nana* in rats. The rest of the compounds were found inactive or showed insignificant activity at doses of 500, 400 or 250 mg/kg.

Based on the cestodicidal activity data (Table 1), the following minimal structural parameters may be defined for optimal activity.

(i) Introduction of electron withdrawing group at R_1 and R_2 positions enhanced the cestodicidal activity whereas electron donating group reduced the activity.

(ii) Presence of pharmacophores with electron withdrawing ability (e.g., NO_2) in phthalimide ring (12-21) is an important factor governing the cestodicidal activity.

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Synthesis and Amoebicidal Activity of Some 2-Methyl-6(8)-alkyl-4-(arylsulphonylhydrazino)quinolines

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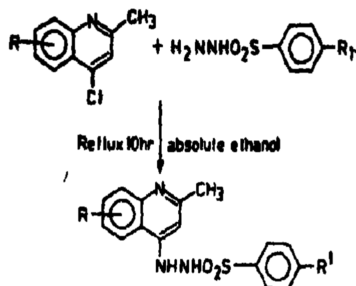
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A series of substituted 4-(arylsulphonylhydrazino)quinolines have been synthesised for studying their amoebicidal activity. All the compounds were screened for amoebicidal activity against *E. histolytica*. Contrary to expectations, no significant amoebicidal activity was observed when testing was done against the axenic culture of *E. histolytica* at a concentration of 125 μg/ml.

A large number of quinoline derivatives like vioform (5-chloro, 7-iodo, 8-hydroxy quinoline), chloroquin and intestopan are well known amoebicides[1,2,3]. Recently, some 4-substituted quinoline derivatives showed enhanced activity against *E.coli*[4,5]. Many substituted sulphonamides also exhibited potent amoebicidal activity[6-11]. It seemed, therefore, of interest to synthesise the title compounds with the object of ascertaining whether the presence of a sulphonyl moiety in quinolines could augment their amoebicidal activity.

Substituted-4-chloroquinolines were refluxed with *p*-substituted arylsulphonylhydrazides in ethanol for 10 hr to furnish the desired quinolines.



Experimental

Melting points were recorded in sulphuric acid bath in open capillary tubes and are uncorrected. Infrared spectra were recorded on Perkin-Elmer-137 spectrometer in KBr.

Substituted-4-chloroquinolines[12] and *p*-substituted arylsulphonylhydrazides[13-16] were synthesised by reported method.

4-(Arylsulphonylhydrazino)quinolines : A mixture of substituted 4-chloroquinoline (0.01 mole) and *p*-substituted arylsulphonylhydrazide (0.01 mole) was refluxed in 50 ml of absolute ethanol for 10 hr. The resulting mixture was concentrated and allowed to stand overnight.

The crystals which separated were filtered and recrystallised from dilute ethanol. The yield ranged between 45 to 65%.

The structure of the compounds was confirmed by their ir spectra. The compounds showed a broad band in the region 3200 – 2700 cm^{-1} characteristic for –NH- and –CH stretching. The ring stretching bands (skeletal bands) occur in the region between 1630-1420 cm^{-1}. Two bands at 1350-1325 cm^{-1} and 1160-1155 cm^{-1} showed the presence of -SO_2NH- group in the molecule. The properties of the compounds thus obtained are summarised in Table 1.

TABLE 1—2-METHYL-6(8)-ALKYL-4-(ARYLSULPHONYLHYDRAZINO)QUINOLINES*

Sl. No.	R	R'	m.p. °C
1.	H	H	282
2.	H	CH_3	218
3.	H	OCH_3	200
4.	H	$NHCOCH_3$	192
5.	8-CH_3	H	178
6.	8-CH_3	CH_3	202
7	8-CH_3	OCH_3	188
8.	8-CH_3	$NHCOCH_3$	218
9.	6-CH_3	H	184
10.	6-CH_3	CH_3	198
11	6-CH_3	OCH_3	190
12	6-CH_3	$NHCOCH_3$	175
13	8-OCH_3	H	141
14.	8-OCH_3	CH_3	128
15.	8-OCH_3	OCH_3	172
16.	8-OCH_3	$NHCOCH_3$	195
17.	6-OCH_3	H	192
18.	6-OCH_3	CH_3	206
19.	6-OCH_3	OCH_3	220
20.	6-OCH_3	$NHCOCH_3$	204

* All the compounds gave satisfactory analyses for C, H, N and S.

Amoebicidal activity : The test compound was dissolved in dimethyl formamide and then diluted with water. It was sterlized by autoclaving for 15 min. Axenic culture of *E. histolytica* (strain 200 :

NIH) was maintained in modified TPS-1 medium containing 0.2% cystine in screw capped tubes at *p*H 6.8. 10000 amoebae/ml of the culture medium, as determined by leuckocytometer count, were inoculated at the bottom of tubes and the tubes were incubated at 37°. Three days old amoeba cultures were used in the experiments described below.

1 ml of a test solution was added to 8 ml of the modified TPS—1 medium in a screw capped tube and incubated overnight. 1 ml of inoculum, containing 10000 amoebae was then added to the bottom of the tube. The tubes were incubated at 37° and amoebicidal end point was determined during 72 hr under an inverted microscope.

In doubtful cases, subcultures were made. In a set of experiments, tubes in duplicates at each dilution of a compound and two controls were included. The standard drugs used were emetine hydrochloride and metronidazole (Flagyl). Unfortunately none of the compounds showed any significant activity at concentration of 125 mg/ml against *E. histolytica*.

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Synthesis of Some 2-Thenoyl-, 5-Bromo-2-thenoyl- and 5-Nitro-2-thenoylamino Acid Derivatives and their Antimicrobial Activity

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The synthesis of 2-thenoyl-, 5-bromo-2-thenoyl- and 5-nitro-2-thenoylamino acid methyl esters (IV-XXVI) and the corresponding hydrazides (XXVII-XLVII) and some dipeptide derivatives (XLVIII-LXVI) is described. Some of the 5-nitro-2-thenoylamino acid methyl ester derivatives, (XIX-XXI and XXIII-XXV), the hydrazides (XLV and XLVII), the dipeptides (LXII-LXIV) and 5-bromo-2-thenoyl-L-tyr-N_2H_3 (XL) and 2-thenoyl-L-val-OMe (VII) and 2-thenoyl-DL-ala-gly-OMe (L) are found to be active against a number of microorganisms.

MANY substituted thiophenes exhibit bacteriostatic, antihistaminic, anaesthetic, antispasmodic, hypnotic, antiviral, anticonvulsant and other pharmacological activities[1-9]. Later, the synthesis of new furan- and thiophene-2-CO-amino acids was reported and the compounds were found to possess some biological activities[10-12]. However, the effect of variation of the functional groups and substitution in both the thiophene and amino acid moieties on the biological and pharmacological activities has not been studied yet.

The present investigation involves the synthesis of some 2-thenoyl-, 5-bromo-2-thenoyl- and 5-nitro-2-thenoylamino acid methyl esters and their corresponding hydrazides and dipeptide derivatives (IV-LXVI) and studies of their microbiological activities.

2-Thenoylamino acid methyl esters (IV-X), 5-bromo-2-thenoylamino acid methyl esters (XI-XVIII) and 5-nitro-2-thenoylamino acid methyl esters (XIX-XXVI) were readily prepared by the reaction of 2-thenoyl chloride (I)[13] or 5-bromo-2-thenoyl chloride (II)[14] or 5-nitro-2-thenoyl chloride (III)[15] with appropriate amino acid methyl ester hydrochloride in methylene chloride-triethylamine medium. The time required for completion of the reactions (3-4 hr) was monitored by tlc. Methylene chloride was found to be the most proper solvent for such coupling reactions. When ether, benzene, THF, dioxane or DMF were used instead of methylene chloride, the products IV-XXVI were obtained in very poor (10-30%) yields and some by-products were isolated. Compounds IV-XXVI were chromatographically homogeneous and did not respond to ninhydrin reaction. Complete acid hydrolysis of IV for 24 hr afforded glycine. The ir spectrum of IV in KBr showed characteristic bands at 3340, 3060 (NH); 1760 (>C=O); 1640, 1560, 1360 (amide I, II and III); 1760, 1480, 1360 and 1050 ($COOCH_3$); 3020, 1420, 1340, 1180, 1050, 890 and 765 cm^{-1} (thiophene and amino acid moieties) confirming its structure. The uv spectrum of IV in ethanol revealed the expected maxima of the thiophene moiety at λ_{max} (log ε) 280 nm (3.95); 227 nm (3.83) and 208 nm (3.74). Analogous peaks were observed in the ir and uv spectra of other compounds concordant with their structures.

The hydrazides XXVII-XLVII were prepared by treatment of the corresponding methyl esters IV-XXVI with hydrazine hydrate in methanol. The products were purified by repeated recrystallization.

2-Thenoyl dipeptide methyl esters (XLVIII-LV), 5-bromo-2-thenoyldipeptide methyl esters (LVI-LXI) and 5-nitro-2-thenoyldipeptide methyl esters (LXII-LXVI) were prepared via the azide method. The hydrazides XXVII-XLVII were converted into the corresponding azides which on coupling with the amino acid esters furnished the dipeptides XLVIII-LXVI which were isolated and purified in the usual manner[16]. Structures of XLVIII-LXVI were assigned on the basis of elemental analyses, chromatographic studies, spot tests and ir and uv spectra.



(Compounds IV-LXVI)

Biological screening results : The antimicrobial activity of compounds IV-LXVI was tested using the hole plate method and filter paper disc method[17-20], and the results compared with the activity of the free acids of (I-III). 5-Nitro-2-thenoyl-gly-OMe (XIX) and 5-nitro-2-thenoyl-DL-ala-OMe (XX) were found to possess high antimicrobial activities against

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TABLE 1—PHYSICAL DATA OF VARIOUS 2-THENOYL-, 5-BROMO-2-THENOYL- AND 5-NITRO-2-THENOYLAMINO ACIDS AND DIPEPTIDE DERIVATIVES (IV-XLVI)

Compd. No.	R	Yield (%)	m.p. (°C)	R_f TLC	$[\alpha]_D^{30°}$
R′=H					
IV	-Gly-OMe	85	93-95	0.83	—
V	-DL-Ala-OMe	80	102-104	0.93	—
VI	-β-Ala-OMe	88	88-90	0.84	—
VII	-L-Val-OMe	89	77-79	0.89	-33.7 (c, 0.6, A)
VIII	-L-Leu-OMe	94	99-101	0.90	-19.6 (c, 0.6, A)
IX	-DL-Phe-OMe	96	111-113	0.83	—
X	-Ach-OMe	84	141-143	0.77	—
R′=Br					
XI	-Gly-OMe	90	96-98	0.76	—
XII	-DL-Ala-OMe	85	110-112	0.82	—
XIII	-β-Ala-OMe	82	100-102	0.81	—
XIV	-L-Val-OMe	81	93-95	0.86	- 5.6 (c, 0.6, B)
XV	-L-Leu-OMe	65	109-111	0.77	-10.5 (c, 0.2, B)
XVI	-DL-Phe-OMe	91	123-125	0.80	—
XVII	-L-Tyr-OMe	80	143-145	0.78	+7.5 (c, 0.4, C)
XVIII	-Ach-OMe	83	150-152	0.84	—
R′=NO_2					
XIX	-Gly-OMe	78	145-147	0.79	—
XX	-DL-Ala-OMe	88	123-125	0.85	—
XXI	-β-Ala-OMe	79	104-106	0.81	—
XXII	-L-Val-OMe	89	200-202	0.83	- 12.5 (c, 0.3, C)
XXIII	-L-Leu-OMe	75	98-100	0.76	+15 (c, 0.6, C)
XXIV	-DL-Phe-OMe	89	141-143	0.73	—
XXV	-L-Tyr-OMe	70	177-179	0.77	- 11 5 (c, 0.3, B)
XXVI	-Ach-OMe	71	143-145	0.83	—
R′=H					
XXVII	-Gly-N_2H_3	92	178-180	0.73	—
XXVIII	-DL-Ala-N_2H_3	87	168-170	0.75	—
XXIX	-β-Ala-N_2H_3	78	228-230	0.72	—
XXX	-L-Val-N_2H_3	86	184-186	0.76	- 6.9 (c, 1, B)
XXXI	-L-Leu-N_2H_3	89	150-152	0.79	+16.9 (c, 0.6, B)
XXXII	-DL-Phe-N_2H_3	95	188-190	0.80	—
XXXIII	-L-Tyr-N_2H_3	83	231-233	0 73	+10 (c, 0.1, A)
R′=Br					
XXXIV	-Gly-N_2H_3	84	228-230	0.60	—
XXXV	-DL-Ala-N_2H_3	93	190-192	0.74	—
XXXVI	-β-Ala-N_2H_3	86	178-180	0 79	—
XXXVII	-L-Val-N_2H_3	83	189-191	0 78	- 11.6 (c, 0.6, B)
XXXVIII	-L-Leu-N_2H_3	96	164-166	0.80	- 30.5 (c, 0.3, A)
XXXIX	-DL-Phe-N_2H_3	87	222-224	0.75	—
XL	-L-Tyr-N_2H_3	90	230-232	0.60	- 13.5 (c, 0.3, A)
R′=NO_2					
XLI	-Gly-N_2H_3	93	201-203	0.81	—
XLII	-DL-Ala-N_2H_3	88	149-151	0.74	—
XLIII	-β-Ala-N_2H_3	80	156-158	0 68	—
XLIV	-L-Val-N_2H_3	58	170-172	0.75	- 25.5 (c, 0.4, A)
XLV	-L-Leu-N_2H_3	95	192-194	0.83	- 50 (c, 0.2, A)
XLVI	-DL-Phe-N_2H_3	94	215-217	0.78	—
XLVII	-L-Tyr-N_2H_3	78	220-222	0.74	- 7.5 (c, 0.2, A)
R′=H					
XLVIII	-Gly-Gly-OMe	62	119-121	0.70	—
XLIX	-Gly-L-leu-OMe	80	116-118	0.74	+30 (c, 1, A)
L	-DL-Ala-gly-OMe	72	154-156	0 79	—
LI	-L-Val-gly-OMe	75	165-167	0.76	- 8.5 (c, 2, A)
LII	-L-Leu-gly-OMe	78	170-172	0.78	+75 (c, 0.35, C)
LIII	-DL-Phe-gly-OMe	70	160-162	0.69	—
LIV	-DL-Phe-L-leu-OMe	59	135-137	0.70	+16.5 (c, 0.6, C)
LV	-L-Tyr-gly-OMe	58	99-101	0.72	+33.5 (c, 0.6, C)
R′=Br					
LVI	-Gly-L-leu-OMe	82	138-140	0.75	+20 (c, 0.5, A)
LVII	-DL-Ala-L-leu-OMe	66	142-144	0.68	- 40 (c, 1, D)
LVIII	-β-Ala-gly-OMe	69	160-162	0.78	—
LIX	-L-Leu-L-val-OMe	60	185-187	0.68	+10 (c, 0.5, D)
LX	-DL-Phe-DL-ala-OMe	73	182-184	0.77	—
LXI	-L-Tyr-gly-OMe	80	122-124	0.73	+16 (c, 0.6, D)

(Table 1 Contd.)

R′ = NO_2					
LXII	-Gly-L-leu-OMe	74	154-156	0.79	+5 (c, 2, B)
LXIII	-Gly-L-tyr-OMe	67	161-163	0.75	−27 5 (c, 0.9, D)
LXIV	-β-Ala-gly-OMe	70	196-198	0.72	—
LXV	-L-Leu-DL-phe-OMe	72	125-127	0.80	−16.5 (c, 0.6, A)
LXVI	-DL-Phe-L-leu-OMe	71	193-195	0 77	−30.5 (c, 1, B)

* $[\alpha]_D^{20}$ were measured in the solvents. (A) = DMF, (B) = methylene chloride, (C) = methanol, (D) = chloroform.
All the compounds gave satisfactory C, H and N analyses

B. subtilis, *B. mycoids*, *B. cereus*, *E. coli*, *S. typhosa* and *P. chrysogenum*. 5-Nitro-2-thenoyl-β-ala-OMe (XXI) and the corresponding -L-leu-OMe (XXIII), -L-tyr-OMe (XXV), -L-tyr-N_2H_3(XLVII) and -gly-L-leu-OMe (LXII) derivatives showed antimicrobial activity against *B. subtilis*, *B. mycoids* and *B. cereus*. 5-Nitro-2-thenoyl-L-leu-N_2H_3 (XLV) was found to be active against *B. subtilis*, *B. mycoids*, *B. cereus* and *P. chrysogenum*. 5-Nitro-2-thenoyl-gly-L-tyr-OMe (LXIII), 5-nitro-2-thenoyl-β-ala-gly-OMe (LXIV), 5-bromo-2-thenoyl-L-tyr-N_2H_3 (XL) and 2-thenoyl-L-val-OMe (VII) inhibited the growth of *B. mycoids* but did not inhibit the growth of *B. subtilis*, *E. coli* and *S. typhosa*. 2-Thenoyl-DL-ala-gly-OMe (L) and 5-nitro-2-thenoyl-DL-phe-OMe (XXIV) produced antimicrobial effects and gave promising results against *B. subtilis* only. The remaining amino acid derivatives were found to be inactive against all the tested microorganisms. The present investigation revealed that substitution in the 5-position of the thenoyl moiety by nitro group in combination with amino acid esters, hydrazides and dipeptide residues gave 5-nitro-2-thenoylamino acid derivatives of high and specific biological properties. However, replacement of the 5-nitro group by 5-bromo group or its removal gave biologically inactive compounds. Other pharmacological studies are in progress.

Experimental

TLC (R_f) was taken on silica gel and developed with *n*-butanol-pyridine-acetic acid-water (30 : 20 : 6 : 24). *o*-Toluidine, benzidine, ninhydrin, silver nitrate and hydroxamate were used as spraying agents and for development (spot reactions). $[\alpha]_D^{20}$ were measured using Carl Ziess polarimeter, 1 dm tube at 20°. Ach = Aminocyclohexane-1-carboxylic acid residue.

2-Thenoyl chloride (I), 5-bromo-2-thenoyl chloride (II) and 5-nitro-2-thenoyl chloride (III) : These were prepared according to the procedures described in the literature[13-15].

General procedure for synthesis of 2-thenoylamino acid methyl esters (IV-X), 5-bromo-2-thenoylamino acid methyl esters (XI-XVIII) and 5-nitro-2-thenoylamino acid methyl esters (XIX-XXVI) : 2-Thenoyl chloride (I) (1.46 g ; 0.01 mole) or 5-bromo-2-thenoyl chloride (II) (2.26 g ; 0.01 mole) or 5-nitro-2-thenoyl chloride (III) (1.92 g ; 0.01 mole) dissolved anhyd. methylene chloride (25 ml) was added dropwise to a solution of the amino acid methyl ester hydrochloride (0.012 mole) or aminocyclohexane-1-carboxylic acid (Ach) methyl ester[21] (0.012 mole) in methylene chloride (80 ml) containing triethylamine (4.5 ml). The reaction mixture was shaken for 30 min at room temperature and then refluxed for 3-4 hr, cooled to 0° and $Et_3N.HCl$ filtered off and methylene chloride (30 ml) added. The mixture was washed with HCl (5%), H_2O, $NaHCO_3$ (5%), H_2O and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residual material recrystallized from benzene, ethanol, *n*-hexane, pet. ether or their mixtures. The products (IV-XXVI) were chromatographically homogeneous (detection with *o*-toluidine or benzidine) and had positive hydroxamate reaction.

General procedure for synthesis of 2-thenoylamino acid hydrazides (XXVII-XXXIII), 5-bromo-2-thenoylamino acid hydrazides (XXXIV-XL) and 5-nitro-2-thenoylamino acid hydrazides (XLI-XLVII) : To amino acid methyl ester (IV-XXVI) (0.01 mole) dissolved in methanol (100 ml), hydrazine hydrate (85%) (2.5 ml ; 0.05 mole) was added and the reaction mixture allowed to stand for 24 hr at 20°. The solvent was removed *in vacuo*, methanol added and re-evaporated several times and the crude product recrystallized from methanol or ethanol-water. The products (XXVII-XLVII) were chromatographically homogeneous (detection with *o*-toluidine) and gave positive silver nitrate reaction.

General procedure for synthesis of the dipeptide methyl esters (XLVIII-LXVI) : The amino acid hydrazide (XXVII-XLVII) (0.006 mole) was dissolved in a mixture of acetic acid (8 ml), 5 *N* HCl (4 ml) and water (40 ml) and cooled to -5°. Sodium nitrite (0.53 g) in water (3 ml) was added and the mixture stirred for 5 min at -5°. The azide was extracted with ethyl acetate (50 ml) and the extract washed successively with H_2O, $NaHCO_3$ (5%) and H_2O and dried (Na_2SO_4). Compounds (XLVIII-LXVI) were prepared by the addition of ethyl acetate solution of the azide to a cooled (-5°) solution of the free amino acid methyl ester (prepared from 0.01 mole of the amino acid methyl ester hydrochloride and 0.9 ml triethylamine as described earlier[16]), and keeping the reaction mixture for 24 hr at 0° and for another 24 hr at room temperature. It was washed successively

with HCl (0.5 *N*), H_2O, $NaHCO_3$ (5%) and H_2O and dried (Na_2SO_4). The solvent was removed and the residual material recrystallized from benzene, ethanol or hexane. All dipeptides (XLVIII-LXVI) were found to be chromatographically homogeneous (detection with *o*-toluidine or benzidine) and gave positive hydroxamate reaction.

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Spectrophotometric Determination of Vanadium with 2 : 2′-Diamino-Diphenyl-Disulphide in Strong Acid Solution

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Vanadium(V) forms a 1 : 1 (M : R) cornflower blue complex with 2 : 2′-diamino-diphenyl-disulphide in 18 *N* sulphuric acid solutions, which passes on to 1 : 2 (M : R) complex with larger amounts of reagents. The absorption maxima of the complexes are 590 nm and 700 nm, respectively. The colour system obeys Beer's law from 8 to 36 ppm with optimum concentration range being the same for vanadium. The percent relative error is 2.72. The compositions of the complexes were determined by the modified Job's and molar ratio methods. The calculated dissociation constants are 1.6×10^{-8} and 5×10^{-9} at 25°. The molar extinction coefficient is 1100 while the Sandell's sensitivity is 0.046 μg/cm². Vanadium can be determined in the presence of large excess of foreign ions, both cations and anions.

DISODIUM maleonitrile dithiolate reacts with vanadium in 0.05 *N* H_2SO_4 to give an intense colour reaction but this method requires that vanadium should be present in tetravalent state[1]. In 10% hydrochloric acid solution vanadium(V) can be determined with 1-naphthylamine, but the colour reaction is not very sensitive, also iron(III) and molybdenum(VI) interfere in the reaction[2]. Acid vanadate solution reacts with 3 . 3′-diamino benzidine but the colour reaction is hindered by anions like phosphate, citrate or fluoride[3].

Vanadox, 2 : 2′-imino-dibenzoic acid reacts with vanadium(V) in concentrated sulphuric acid medium[4] to form a coloured complex. The author has listed certain reagents which may be used for estimation of vanadium(V) but none of them has been applied in determination of vanadium from complex mixtures such as alloys or ores.

The present paper describes mixed 1 : 1 and 1 : 2 (M : R) complex formation of vanadium(V) with 2 : 3′-diamino-diphenyl-disulphide in 18 *N* H_2SO_4. Vanadium can be determined in alloys and ores as large number of cations, anions and masking agents such as fluoride, citrate, oxalate and EDTA do not interfere in the determination.

Experimental

Apparatus, reagents and solutions: Optical densities of the solutions were measured in 1 cm quartz cells in a Hilger Uvispek spectrophotometer.

Preparation of O:O′-diamino-bisphenyl-disulphide[5]: *Ortho*-aminobenzene thiol (0.1 mole) was dissolved in 50% EtOH and air was passed through the solution in small bubbles for 72 hr. The solution, with some suspended solid, reagent, was freed from alcohol and cooled when crystals of reagent appeared. This was filtered, washed with water and dried by suction. The product was crystallised from 90% EtOH, m.p. 65°. Analysis: Found: C, 57.95; H, 4.75; N, 11.02. Calcd. for $C_{12}H_{12}N_2S_2$; C 58.06; H, 4.83; N, 11.29%.

A 2% (w/v) reagent solution was prepared i[n] acetonitrile (Riedel de Haen).

A standard vanadium(V) solution was made b[y] dissolving known weight of preheated ammoniu[m] vanadate in dilute ammonium hydroxide solutio[n]. The vanadium content was checked by titratio[n] with EDTA by complexometric method[6]. Weak[er] solutions were obtained by proper dilution.

Sulphuric acid solution, 18 *N*, was prepared b[y] diluting in 1 : 1 proportion, analytical grade con[c.] sulphuric acid with twice distilled water.

Solutions of diverse ions were prepared fro[m] the metal salts or from the sodium or potassiu[m] salts of anions in twice distilled water and estimate[d] according to standard methods.

Results and Discussion

Spectral transmittancy curve: 400 μg of vana[-] dium(V) was taken in a 25 ml volumetric flask an[d] 5 ml of 18 *N* H_2SO_4 solution and 5 ml of 2% reage[nt] solution were added to it. The mixture was warme[d] on water bath for 10 min. It was cooled to roo[m] temperature and the volume was made up with 18 [N] sulphuric acid solution. A reagent blank w[as] identically made in which the metal solution w[as] not added. Absorbances of the reagent and t[he] test solutions with water blank and of the te[st] solution with reagent blank were taken. The cur[ve] in Fig. 1 shows that the deep blue coloured compl[ex] of vanadium and the reagent has absorption maxi[ma] at 590 nm and 700 nm.

Effect of acid concentration: To study the effe[ct] of acid concentrations, different amounts of 18 [N] sulphuric acid solution were added, to mainta[in] desired acid concentrations, to 400 μg portions [of] vanadium(V) along with 5 ml portions of reagen[t]

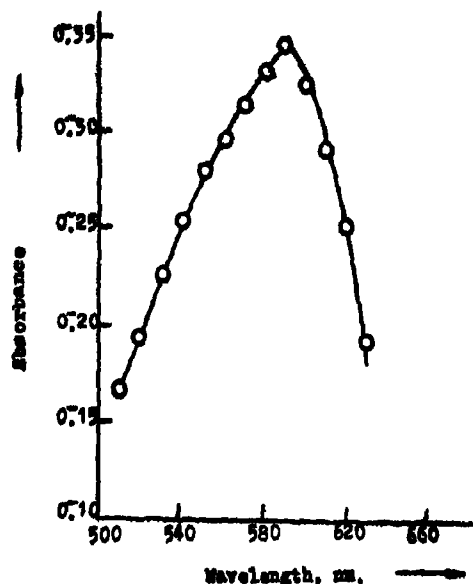


Fig. 1. Spectral transmittancy curve.

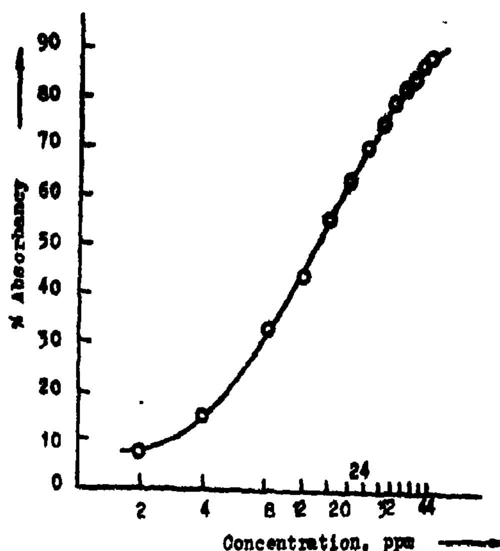


Fig. 2

Each mixture was heated on water bath, cooled and volume made up with sulphuric acid solutions of the desired normality. Absorbance measurements of these different solutions show that the absorbances of the colour system at 590 nm increased upto an acidity of 12 *N* and remained constant with higher acid concentrations. All subsequent measurements were made in an optimum acid concentration of 18 *N*.

Effect of reagent : The absorbances of the colour system increased with the addition of increasing amounts of 2% reagent solution upto 3.0 ml. It remained constant upto 5.0 ml reagent solution in the mixture.

Effect of time : The vanadium-disulphide colour system in 18 *N* H_2SO_4 is stable for 24 hr; light blue crystals appear thereafter and absorbances decrease rapidly.

Beer's law, optimum range and accuracy : Beer's law is obeyed by the colour system for 8.0 to 36.0 ppm of vanadium.

The optimum range for accurate determination of vanadium was obtained by plotting precent absorbancy at 590 nm against log concentration according to Ringbom[10]. Fig. 2 shows that the steepest portion of the curve is from 8.0 ppm to 36 ppm of vanadium which is the optimum range; the percent relative error per 1% absolute photometric error for this range is 2.72% as obtained according to Ayres[11].

Sensitivity and molar extinction coefficient : Spectrophotometric sensitivity was calculated according to Sandell[12] from Beer's law curve and found to be 0.46 μg vanadium(V)/cm^2 where the molar extinction coefficient with the disulphide is 1100.

Effect of diverse ions : Solutions of varying concentrations of foreign ions were mixed with 400 μg of vanadium(V) solutions and the colour was developed as given in the procedure. It was found that large excess (800 μg) of lithium, magnesium, calcium, ammonium, rare-earths, aluminium, titanium(IV), zirconium, thorium, iron(II and III), molybdenum(VI), tungsten(VI), platinum(IV), rhodium(III), iridium(III) and common anions like chloride, bromide, iodide, nitrate, phosphate, arsenate, fluoride, oxalate and citrate had no effect on the determination of vanadium. Longer period of heating is necessary for full colour development when borate is present. Copper, nickel, cobalt, palladium(II) and tartrate interfere.

Composition of the complex : It was found that the metal combines with the reagent in a metal-ligand ratio of 1 : 1 which passes on to the ratio of 1 : 2 (M R) with excess of reagent. This was found out by the modified method of Job[5,6]. Equimolar solutions of vanadium and the reagent were taken. Complimentary mixtures of vanadium and reagent solutions were mixed in different flasks and colour was developed. Their absorbances were measured against water as blank. The portion of extended scale of the plot in the Fig. 3 shows that vanadium combines with ligand in a ratio of 1 : 2 and rest of the portion show that vanadium also combines with the reagent in 1 : 1 ratio.

The above observations were confirmed by the molar ratio method[9]. A constant concentration of vanadium was mixed with different volumes of reagent to maintain the ratios of metal to reagent different in each study. The curve in Fig. 4 show breaks at the molar ratios of 1 : 1 and 1 : 2 (M : R).

Degree of dissociation or instability constant : The degrees of dissociation, α_1 and α_2, obtained by the method of Harvey and Manning[13] are, 0.179 and 0.042, respectively, for 1 : 1 and 1 : 2 complexes. The dissociation constants were calculated according

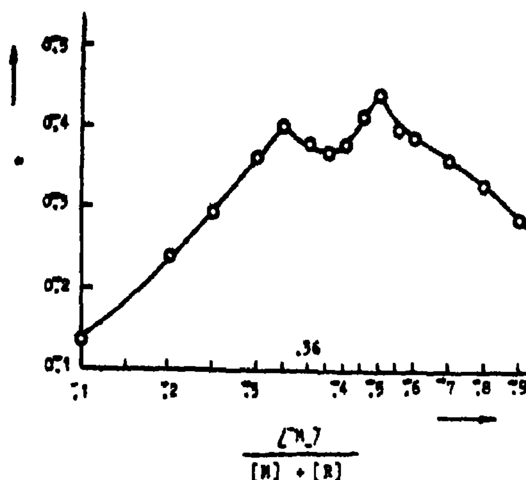


Fig 3 Job's method of composition

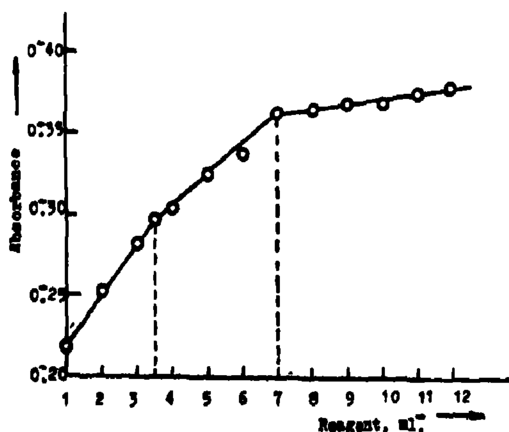


Fig. 4. Molar-ratio method of composition.

to the equation, $K=\frac{(m\alpha C)^m (n\alpha C)^n}{C(1-\alpha)}$, where m and n are the numbers of metal ions and ligand molecules involved in the complex formation, C is the molar concentration and α is the degree of dissociation, given by $\alpha=\frac{Am-As}{Am}$; where Am is the absorbance with large excess of reagent and As is the same with stoichiometric amount of reagent in the complex. The dissociation constants at 25° are 1.6×10^{-8} for 1 : 1 complex and 5×10^{-9} for the complex with metal to ligand ratio of 1 : 2.

Estimation of vanadium in alloy and ore : High-speed steel, BAS 646, 0.5 g was taken in a beaker and digested with 20 ml of 1 : 4 sulphuric acid. When the sample dissolved, 5 ml of concentrat nitric acid was added and heated to medium-stro fumes of SO_3. The mass was cooled and dilut with double-distilled water and oxidised with a fi drops of 0.1 *N* $KMnO_4$ solution in cold. Tl product was stirred with excess NaOH soluti (15% w/v) and boiled for a few minutes. Residue Fe(III), Ti and Mn hydroxides and oxide w filtered off and washed with hot water. The filtra was collected and the residue was dissolved in h HCl (1 : 2) and reprecipitated as before. Tl combined filtrates were made upto 100 ml in volumetric flask with twice distilled water. A aliquot was taken for spectrophotometric analysi The result is given in Table 1.

Titaniferrous magnetite (magnetite+ilmeni natural mixture) ore, ground to 200 mesh w mixed with 10-12 times its weight of anhydro sodium carbonate and a little of potassium nitrat The mixture was fused in a platinum crucible an was kept in the fused state for 15 min. It w cooled and leached in 50 ml hot water. Th product was boiled to precipitate all the hydroxid and the residue was filtered. The filtrate was finall made upto 100 ml in a volumetric flask. An aliqu was taken for the analysis of vanadium. The resul is given in Table 1.

Table 1—Statistical Average of Three Readings for each Sample

	Sample	% Vanadium as certified	% Vanadium found
1	High Speed steel BAS 646	1.99	1.985
2.	Titaniferrous magnatite ore	1.05	1.019

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Determination of Aluminium in Iron Ores

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Investigation was undertaken to provide a widely applicable analytical method for the routine determination of aluminium content of iron ore. Published methods tend to be tedious, time consuming and inaccurate. A procedure, which over-comes these difficulties to a large extent, based on preliminary separation of iron by the ion exchange method (Dowex-1) and colorimetric determination of Al by 8-hydroxy quinoline in $CHCl_3$ at pH 8.5-9.5 is described.

ALUMINIUM is a common constituent of iron ore and is usually present in small amounts. The determination of aluminium in iron ores is important for the evaluation of the ores for metallurgical purposes. Although many methods have been recommended for estimating Al in iron ores, they are not reliable. The difficulties are the separation of aluminium from the major element Fe, and the adoption of a suitable method for the estimation of Al. The classical methods for determination of Al in iron ores are tedious and inaccurate. Lang and Reifer determined Al in presence of Fe by using tartrate and KCN[1]. Lundell[2] and Kassner and Ozier[3] determined Al gravimetrically as aluminium oxinate in the presence of Ti, V, etc. But this procedure must be carefully performed to obtain accurate values. Weberly and Bassett[4] adopted mercury cathode electrolysis to separate Fe. The method is cumbersome in manipulation and time consuming. Moreover, a method that needs a lengthy separation of Fe and Ti is not reliable and exact in selection of a procedure. The systematic study on the colorimetric determination of Al as aluminium oxinate made by Gentry and Sherrington[5] revealed the role of pH and interferences of other elements. To apply colorimetric method, a preliminary separation of Al from iron[6,7] is necessary. Attempts made in various laboratories to apply the separation led to erratic results. Kassner and Ozier adopted an extractive colorimetric method in the presence of iron by using an ammonical solution containing tartrate and KCN.

The present communication describes a convenient and accurate method for routine determination of aluminium in iron ores by the combined ion exchange solvent extraction separation of Al as aluminium oxinate at pH 8.5-9.5 in $CHCl_3$ and the measurement of its absorbance at 390 nm.

Experimental

Reagents and solutions : All the chemicals used were of analytical reagent grade. Stock solution of aluminium (100 μg/ml) was prepared by dissolving potassium alum, $KAl(SO_4)_2.12H_2O$ in 0.25 *M* HCl. 1% solution of 8-hydroxy quinoline (BDH) in $CHCl_3$ (E. Merck) was used as the complexing agent.

Equipment : Spectronic-20, Bausch and Lomb spectrophotometer was used for the measurements of absorbance at 390 nm using a glass cell of 1 cm path length.

Anion exchange technique : Dowex 1-X8 resin (200 mesh) in the chloride form was used as a strong base anion exchanger. A slurry of the resin in water was poured into a 25 ml burette fitted with a glass wool plug at the bottom. The column had an internal diameter 1 cm and a length of 10 cm. The effluent flow rate was 1 ml per min.

Procedure : 2.5 g sample of the finely ground iron ore was weighed in a 250 ml beaker, treated with 30-35 ml conc. HCl (sp. gr. 1.18) and heated slowly on a hot plate until the ore dissolved. The glass cover was rinsed, the solution evaporated to dryness and the residue baked for 1 hr. The baked residue was treated with 100 ml dilute HCl (1 : 1) and warmed to a clear solution and filtered. The filtrate was preserved. The residue was ignited in platinum crucible, cooled and weighed. It was treated with HF to volatilize silica, ignited, cooled and weighed again to determine silica content. The silica free residue was fused with 2 g Na_2CO_3 and extracted with 5% HCl solution. The extracts were added to the preserved filtrate and the volume made up to 500 ml. 20 ml aliquot, equivalent to 0.1 g sample, was evaporated to dryness in 50 ml beaker, dissolved in 5 ml 9 *M* HCl and passed through the column at the rate of 1 ml/min and collected in a 100 ml volumetric flask. The resin was then washed with 50 ml of 9*M* HCl in 4 instalments and the eluates collected in the same flask. The Al solution was made up to 100 ml volume and used for analysis.

10 ml water, 0.2 g tartaric acid and 1 ml 3% H_2O_2 were added to 10 ml aliquot of the Al solution in a separatory funnel and shaken. Then 10 ml NH_4OH was added. The pH was adjusted to

8.9-9.5, 10 ml of 1% oxine solution was added, the whole was shaken for 2 min and allowed to stand for 10 min. The $CHCl_3$ layer was taken in 25 ml vol flask. The aqueous layer was extracted with another 10 ml $CHCl_3$ and finally 5 ml $CHCl_3$. The combined $CHCl_3$ extracts were diluted to 25 ml with $CHCl_3$ and the absorbance was measured at 390 nm. Al content was determined from calibration curve prepared by measurements with known amounts of Al. A blank was run in which 10 ml of water was used in place of the 10 ml Al solution. The results are shown in Table 1.

TABLE 1—DETERMINATION OF ALUMINIUM

Iron Ore Samples	Fe%	Al% (by conventional classical method)*	Al% (by the present method)
S_1	68.67	1.95	1.90
S_2	63.94	1.80	1.88
S_3	65.90	1.45	1.51
S_4	68.68	0.40	0.50

*Fe separation by Dynacath Hg-electrolysis, Ti separation by NaOH and Al determination in the filtrate as Al-oximate at pH 5-6.

The above combined procedure was repeated with synthetic Al solution containing Fe and Ti. The results are shown in Table 2.

TABLE 2—DETERMINATION OF ALUMINIUM IN A SYNTHETIC MIXTURE

Fe (taken) mg	Ti (taken) mg	Al (taken) µg	Al (found) µg	% error
56	2	400	380	−5%
56	2	800	780	−3%

Results and Discussion

Table 1 shows that the results obtained by the two procedures were quite satisfactory. Table 2 shows the recovery of Al in a synthetic mixture, prepared from known quantities of Fe, Ti and Al. The concentration of Fe and Ti normally found in iron ores had no apparent effect on Al recovery from ion exchange separation and could therefore be disregarded as a source of interference. The amount of Al found (Table 2) was slightly less than the amount added. This method has the following advantages.

(a) Iron forms anionic chloro complex in 9 *M* HCl and is retained strongly on the anion exchanger. Al^{3+} and Ti^{4+} pass out through the column and are collected as eluates[7,8,9]. The interference of titanium in subsequent colorimetric determination of aluminium as oximate complex in $CHCl_3$ is removed by adding H_2O_2 so as to form peroxy titanic acid retained in the aqueous phase.

(b) The time required to effect separation of iron by ion exchange and subsequent spectrophotometric determination of Al is far less than the conventional classical method.

(c) The method is selective and sensitive.

(d) Quite a large number of samples can be analysed for Al by setting up several ion exchange columns and using 100 ml volumetric flasks and separating funnels. The conventional classical method requires costly apparatus and much longer time to effect similar Fe and Ti separations.

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NOTES

Studied on Heteropoly 6-Ammonium Molybdochromate

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THE synthesis and preliminary studies of 12-heteropoly molybdochromate have been reported by Mishra *et al*[1]. Kazanskii and co-workers[2] have synthesised some interesting hexamolybdochromate complexes. Older literature[3] contains only a few report of molybdochromates without distinguishing the compounds to be true heteropoly complexes. The synthesis only of $(NH_4)_6$-$[CrMo_6O_{24}].10H_2O$ was reported[4] in our previous communication but the details are discussed here. Ammonium molybdate (0.05*M*, 50 ml) together with glacial acetic acid (20 ml) and potassium dichromate solution (0.05*M*, 40 ml) was refluxed for 3 hr, evaporated to crystallization and left in atmosphere for several days. An orange coloured flaky powdery compound separated after 5 days. The compound was recrystallized thrice from hot water. Analysis of the compound was carried out by usual chemical and colorimetric methods. Chromium interferes[6] with the estimation of molybdenum with α-benzoin oxime and hence had to be separated first. For this purpose molybdenum was quantitatively separated[7] from the solution of the compound as molybdenum sulphide by passing H_2S at 5° at reduced pressure for 45 min in presence of formic acid and filtered. The chromium in the filtrate was estimated as lead chromate[8]. The precipitated molybedenum sulphide was dissolved[7] in conc. HCl with minimum amount of $KClO_3$, diluted, made alkaline and the molybdenum estimated with α-benzoin oxime. Molybdenum was also estimated colorimetrically by potassium thiocyanate method[9]. Nitrogen and hydrogen were estimated by element estimation technique. Analysis: Found: Cr, 4.02; Mo, 46.72; N, 6.62; H, 3.32. Calcd. for $(NH_4)_6$-$[CrMo_6O_{24}].10H_2O$; Cr, 4.22; Mo, 46.90; N, 6.68; H, 3.58%. The formulation of the compound was according to Evans[10].

Thermoderivatographic studies: Clark[11] first made some thermal studies with a few heteropoly molybdates and tungstates. Heteropoly compounds, which can be regarded as condensation inorganic polymers[12], have further been studied by West and Audrith[13] from their depolymerization point of view. The thermoderivatographic studies of the present compound show that 2 molecules of water are eliminated at 60° with an endothermic peak. Another 2 molecules of water and 6 molecules of ammonia are eliminated at 160 and 250° with two successive endothermic peaks. No loss in weight was found upto a certain range of temperature. At 450° the remaining 6 molecules of water are eliminated with an exothermic peak clearly indicating complete break-down of the crystal lattice of the compound into the lower oxides of the constituent metals, which have been confirmed by analysis and ir spectra of the last product. Obviously these 6 molecules of water are acting as water of constitution of the compound. IR spectra of the compound ignited upto 260°, indicates complete removal of ammonia molecules in this stage, showing absence of bands at 1405 and 3100 cm^{-1} corresponding to N-H stretching and deformation frequency of NH_4^+ ion.

Infrared spectral studies: Tsigdinos[14], Sharpless[15] and Brown[16] have examined infrared spectra of some of the heteropoly compounds. Infrared spectra of the prepared compound have been recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer, model 577 grating infrared spectrophotometer. The spectrum is recorded in KBr pellets. The peaks are observed at 3190, 1525, 1405, 1090, 945, 900, 880, 740, 615, 510, 365, 245, 220, 200 cm^{-1}. The peak at 3190 (antisymmetric and symmetric O-H stretching modes[17]) is due to the presence of lattice water[18]. The peaks at 1405 and 1525 cm^{-1} can also be attributed to lattice water (H-O-H bending mode[18]). Recently Elsken and Robinson[19] have shown that lattice water also absorbs at the lower frequency region (600-400 cm^{-1}) owing to liberational modes. So, it may be considered that bands at 615, 510 cm^{-1} are due to the presence of lattice water in either of the three fundamental modes of free water molecules. The strong bands at 945, 900 and 740 cm^{-1} may be due to M-O and M-O-M linkage[18] (M = Mo). The strong bands at 880 and 365 cm^{-1} are due to the tetragonal CrO_4^{2-} ions. The absorption at lower frequency region, 245, 220 or 200 cm^{-1}, may be attributed to the elongated stretching of compact M-O-M bridging of addenda atoms. The band at 1405 cm^{-1} corresponds to N-H stretching frequency[20]. The broad band at around 3100 cm^{-1} corresponds to the deformation frequency of NH_4^+ ion[20].

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Metal Complexes of Sulfur-Nitrogen Chelating Agents : Organotin(IV) Derivatives of Diethylaminomethyl Ester of 2-Amino-1-cyclopentene-1-carbodithioic Acid

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METHYL ester of 2-amino-1-cyclopentene-1-carbodithioic acid is found to be a good chelating agent for several metal ions forming six-membered chelates[1-6]. In view of antifungal properties[1,6,7-11] of both the ester and the organotin(IV) compounds, it was considered interesting to synthesize organotin(IV) derivatives of another ester, diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid, $H_2N\overline{CCH_2CH_2CH_2C}C(S)SCH_2N(C_2H_5)_2$ (LH), and examine the structural features as well as the biological activities of these organotin(IV) complexes.

Experimental

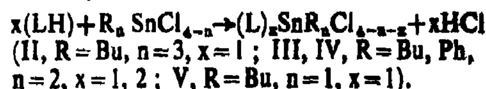
All manipulations were carried out under rigorous dry conditions. Solvents were dried by the standard techniques. Diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid was prepared by the literature method[9,12]. Monobutyltin trichloride (93°/10 mm), dibutyltin dichloride (153-156°/5 mm), tributyltin chloride (102°/0.5 mm), dimethyltin dichloride (185-190°/760 mm) and diphenyltin dichloride (93°/10 mm) were distilled before use. Dimethyltin(IV) diisopropoxide was prepared by the sodium isopropoxide method. Tin, sulfur and chlorine were estimated gravimetrically and nitrogen by Kjeldahl method. Molecular weights were determined cryoscopically in benzene. The ir spectra were recorded on a Perkin-Elemer 621 spectrophotometer as neat and nujol mull in the range 4000-200 cm^{-1}. PMR spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard.

General method of preparation of the organotin(IV) complexes of diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid : Organotin(IV) chlorides (Bu_3SnCl, Bu_2SnCl_2, $BuSnCl_3$ and Ph_2SnCl_2), diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid and triethylamine (in appropriate molar ratios) were taken in THF (~60 ml) and the contents stirred at room temperature (~32°) Triethylamine hydrochloride was filtered out and the solvent removed *in vacuo*. The products (Table 1, Sl. No. 1 and 4-8) were crystallized from benzene-hexane and dried at 50°/0.1 mm/1 hr.

Preparation of the dimethyltin(IV) complexes : Dimethyltin(IV) diisopropoxide and diethylaminomethyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid taken in appropriate molar ratios in THF (~60 ml) were heated under reflux. After completion of the reaction, the solvent was removed *in vacuo* and the products dried at 50°/0.1 mm/1 hr (Table 1, Sl. No. 2 and 3).

Results and Discussion

Tributyltin(IV), dibutyltin(IV), monobutyltin(IV) and diphenyltin(IV) derivatives [compounds (II-V)] of diethylamino-methyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid, (I), have been obtained by the reactions of the appropriate metal chlorides in the presence of triethylamine (Table 1, Sl. No. 4-8).



$$x(LH)+R_n\,SnCl_{4-n} \rightarrow (L)_xSnR_nCl_{4-n-x}+xHCl$$
(II, R = Bu, n = 3, x = 1 ; III, IV, R = Bu, Ph, n = 2, x = 1, 2 ; V, R = Bu, n = 1, x = 1).

Since the dimethyltin(IV) analogue could not be obtained in pure state, corresponding diisopropoxide was used as the starting material. Dimethyltin(IV) isopropoxide reacted readily to give the desired product (Table 1, Sl. No. 2 and 3.),



$$Me_2Sn(OPr^i)_2+nLH \rightarrow Me_2Sn(OPr^i)_{2-n}(L)_n+nPr^iOH \;(n = 1 \text{ and } 2).$$

Organotin(IV) compounds synthesised are dark brown shining foamy crystalline solids except tributyltin(IV) and monobutyltin(IV) complexes which are brown distillable liquids. All compounds

TABLE 1—ORGANOTIN(IV) DERIVATIVES OF DIETHYLAMINOMETHYL ESTER OF 2-AMINO-1-CYCLOPENTENE-1-CARBODITHIOIC ACID

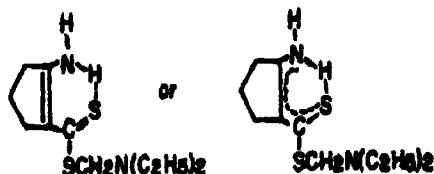
Sl. No.	Products* (nature)	m.p. or b.p./mm (°C)	Analysis %* Found (Calcd.) Sn	S	N	Cl
1.	$C_{23}H_{46}N_2S_2Sn$ (Dark brown low melting solid)	128-30/0.02	22.77 (22.26)	11.77 (12.02)	5.12 (5.25)	–
2.	$C_{16}H_{32}ON_2S_2Sn$ (Dark brown foamy crystalline solid)	118-20 (d)	26.76 (26.81)	14.74 (14.21)	6.49 (6.31)	–
3.	$C_{24}H_{44}N_4S_4Sn$ (Dark brown foamy crystalline solid)	107-8 (d)	18.64 (18.68)	20.45 (20.18)	8.84 (8.82)	–
4.	$C_{30}H_{56}N_4S_4Sn$ (Dark brown foamy crystalline solid)	81-83 (d)	16.37 (16.50)	17.91 (17.82)	7.49 (7.78)	–
5	$C_{19}H_{37}N_2S_2ClSn$ (Dark brown foamy crystalline solid)	107-10 (d)	23.94 (23.20)	12.27 (12.53)	5.59 (5.48)	6.70 (6.93)
6.	$C_{23}H_{29}N_2S_2ClSn$ (Dark brown foamy crystalline solid)	116-18 (d)	21.98 (21.52)	11.31 (11.62)	5.20 (5.08)	6.56 (6.43)
7.	$C_{34}H_{48}N_4S_4Sn$ (Dark brown foamy crystalline solid)	121-22 (d)	15.72 (15.68)	16.74 (16.89)	7.46 (7.38)	–
8.	$C_{15}H_{28}N_2S_2Cl_2Sn$ (Brown low melting solid)	110-15/0.4	23 80 (24.22)	13.65 (13.00)	5.65 (5.72)	14.78 (14 46)

* Yield, 90-98% , compounds are monomeric as determined cryoscopically , d = decompose

* In sample cases, C and H analyses were checked (values in parentheses are the calculated ones), Sl. No. 1, Found (%), C, 50 95 (51.76), H, 8 81 (8.70) and Sl. No. 4, Found (%), C, 51.10 (50.07), H, 7.68 (7.85).

are monomeric in nature as found cryoscopically in benzene except dimethyltin(IV) complexes whose poor solubility prevented the determination of their molecular weights.

In the infrared spectra of the diethylaminomethyl ester, the presence of a broad band of ν(N–H) at 3245 cm^{-1} and the absence of ν(S–H) band at 2550-2650 cm^{-1} region reveal the following delocalized structure for the ester[3]. The absence of ν(S–H) even in the solution spectra reveals the absence of the enolized form of the ligand.



I

The modes of ν(C=S) which appear in I at 1265, 1155 cm^{-1} along with ν(C=N)[3], and at 725 cm^{-1}, exhibit a negative spectral shift[1,3,5,18] of the order of 15-20 cm^{-1} in all organotin(IV) derivatives, suggesting the bidentate nature of the ligand.

In all the organotin(IV) derivatives ν(Sn–S)[14-19] absorptions can be seen at 385±5 and 325±5 cm^{-1} as two sharp weak bands. ν(Sn–Cl)[20-22] frequencies in diorganochlorotin(IV) and butyltin(IV) compounds appear in the region 300-350 cm^{-1}. The characteristic bands of ν_{as}(Sn–C) at 590 and ν_s(Sn–C) at 500 cm^{-1} in tributyltin(IV) compound, (II), suggest that all the three butyl groups are not in one plane[23,24] revealing trigonal bipyramidal structures for them. In diorganotin(IV) derivatives the presence of more than one ν(Sn–C)[25] bands in the region 580-600 and 500-515 cm^{-1} assignable to ν_{as}(Sn–C) and ν_s(Sn–C) suggests a *cis*-octahedral geometry for the *bis*-complexes. The characteristic band of ν(Ph–Sn)[26] appears at 1070 cm^{-1} in diphenyltin(IV) complexes. In the case of monobutyltin(IV) compounds ν_{as}(Sn–C) and ν_s(Sn–C) modes can be assigned at 595 and 535 cm^{-1} respectively[26].

PMR spectrum of the ligand[3] shows the following signals (in τ scale), SCH_2N (4.92, singlet), CH_3 (8.88, triplet) of the ethyl group, 3 and 5-CH_2 protons of the ring and CH_2 protons of ethyl group (6.8-7.5, multiplet), 4-CH_2 (8.16, quintet) and NH (4.19, broad signal). In all the organotin(IV) complexes 4-CH_2 proton signals remain at the same position while 3- and 5-CH_2 and SCH_2 protons undergo a slight upfield shift due to chelation[1,4,5].

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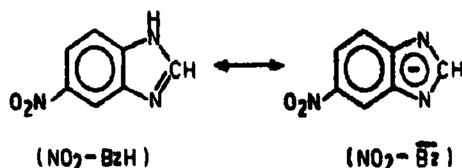
Complexes of 5-Nitrobenzimidazole with Some Metal Ions

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COMPLEXES of various transition metal ions with benzimidazole and substituted benzimidazoles have been reported[1-6]. 5-Nitrobenzimidazole (NO_2 – BzH) contains an electron withdrawing NO_2 group capable of reducing electron density at donor benzimidazole nitrogens through hyperconjugation. It is, therefore, expected that donor ability of benzimidazole nucleus will be affected appreciably. In



the present note, the preparation and characterisation of Ni(II), Co(II), Zn(II), Cu(II), Cd(II) and Hg(II) complexes with NO_2-BzH are reported. The effect of NO_2 substitution on donor ability of benzimidazole nucleus is also discussed.

Experimental

Preparation of complexes : $M(NO_2-Bz)_2.nH_2O$ ($M=Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} or Hg^{2+} and $n=0$ but 2 in case of Ni^{2+}) : An aqueous ethanolic solution of the metal acetate was treated with hot ethanolic solution of the ligand (1 : 2.5 molar ratio) and pH was raised to 7-8 by adding a few drops of dilute ammonia when the neutral complex separated. The product was digested on a steam bath for about half an hour, filtered, washed with ethanol and dried at ~ 100° in an air oven.

$M(NO_2$-$BzH)_2X_2$, ($M=Cu^{2+}$ or Hg^{2+} and $X=Cl^-$ or Br^-) : Methanolic (or acetone) solution of metal halide (0.005 mole in 50 ml) was treated with stoichiometric proportion of ligand dissolved in the same solvent. From resulting solution, the dihalo complexes separated gradually. The product was filtered, washed with cold methanol and dried in air. The determination of magnetic moment values, solid reflectance and ir spectra of the complexes were made as reported earlier[2,3].

Results and Discussion

The neutral *bis* ligated complexes $M(NO_2$-$Bz)_2$.nH_2O are insoluble in water and organic solvents like methanol, ethanol, chloroform, acetone etc., indicating their polymeric nature. Excepting Cu^{2+} and Hg^{2+}, the dihalo or other acidic complexes of other common metals like Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, VO^{2+} etc. could not be isolated in solid state, similar to benzimidazole[5,6] and alkyl benzimidazole[7,8], probably due to weak metal-ligand bonding caused by low electron density on imidazole nitrogen of NO_2-BzH molecule.

The dihalo complexes $M(NO_2-BzH)_2X_2$ ($M=Cu^{2+}$ or Hg^{2+}) are slightly soluble in ethanol, dioxane, dmso and DMF. The molar conductance values of complexes in DMF solution are negligible (Λ_M 8-15 mol^{-1} ohm^{-1} cm^2) indicating the coordination of halogen atoms in these complexes.

Zn(II), Cd(II) and Hg(II) complexes are diamagnetic and do not display electronic absorption band in the visible region. On the basis of stoichiometry, four coordinated tetrahedral structure is tentatively suggested for Zn(II), Cd(II) and Hg(II) complexes since tetrahedral geometry is the more preferred geometry for these metal ions[9].

The colour, magnetic moment value (μ_{eff} 4.71 B.M.) and reflectance spectrum of $Co(NO_2$-$Bz)_2$ decidedly indicate its pseudotetrahedral structure[10,11]. A strong band at 18020 cm^{-1} is assigned $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition and a shoulder at 18,850 cm^{-1} is due to splitting of $^4T_{1g}$ (P) term under the influence of spin-orbit coupling in tetrahedral field[12].

$Ni(NO_2$-$Bz)_2(H_2O)_2$ displays magnetic moment value, *ca* 2.96 B.M., similar to octahedral or distorted octahedral nickel(II) ions[13]. The diffused reflectance spectrum in the region 28,500-10,000 cm^{-1} exhibits a weak and broad band at

TABLE—1

Complex ($LH=NO_2-BzH$)	Colour	% Metal Found (Calcd.)	% Nitrogen Found (Calcd.)	μ_{eff} (B.M.) (at 304 K)	Spectral band position (cm^{-1})
CoL_2	Pink	16.21 (15.88)	21.61 (21.94)	4.71	18850 sh, 18020 s
CuL_2	Greenish yellow	16.24 (16.88)	21.21 (21.61)	1.88	16010-14760 br
$NiL_2(H_2O)_2$	Yellowish green	13.81 (14.01)	20.13 (20.06)	2.98	25870 sh, 15880 w
ZnL_2	Cream	17.01 (16.78)	21.41 (21.58)	Dia.	–
CdL_2	Cream	25.46 (25.75)	19.42 (19.25)	Dia.	–
HgL_2	Cream	37.81 (36.28)	16.31 (16.02)	Dia.	–
$Cu(LH)_2Cl_2$	Bluish green	13.81 (13.79)	18.11 (18.24)	1.92	15150-13500 br
$Cu(LH)_2Br_2$	Brown	11.71 (11.56)	15.07 (15.28)	1.84	14280-12500 br
$Hg(LH)_2Cl_2$	Cream yellow	33.21 (33.58)	14.21 (14.06)	Dis.	–
$Hg(LH)_2Br_2$	Cream yellow	29.66 (29.23)	12.11 (12.41)	Dis.	–

Results of halogen analyses in complexes correspond with the required values.

13,380 cm^{-1} and a shoulder at 25,370 cm^{-1} assignable to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3A_{1g}$(P) transitions, respectively[14]. From the relations of different ligand field parameters with the energies of ν_2 and ν_3 transitions the values of 10 Dq and B have been calculated and are found to be 9523 and 810 cm^{-1}, respectively[15].

Copper(II) complexes display magnetic moment values between 1.84 and 1.92 B.M. indicating that these complexes are magnetically dilute[16]. The reflectance spectrum of $Cu(NO_2-Bz)_2$ displays a broad and weak band at 16,130-14,720 cm^{-1} assignable to combination of ${}^2B_{2g} \rightarrow {}^2B_{1g}$ plus ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transitions in distorted octahedral field[17]. The ligand field bands in dihalo complexes CuL_2X_2 ($L=NO_2-BzH$ and X=Cl or Br) are observed at low energy (15,150-12,500 cm^{-1}) and are assymetric in nature. The occurrence of d–d transition at low energy and assymetric nature of spectral band indicate that tetragonal distortion is more in dihalo complexes than that of $Cu(NO_2-Bz)_2$.

The ir spectrum of ligand displays (N–H) stretching band at 3258 cm^{-1} which disappears in its neutral complexes $M(NO_2-Bz)_2$ ($M=Co^{2+}$, Cd^{2+}, Zn^{2+}, Cu^{2+} or Hg^{2+}) indicating that (N–H) proton has been deprotonated in its complexes. The diaquo complex $[Ni(NO_2-Bz)_2(H_2O)_2]$ displays a broad and medium band at 3300-3450 and a shoulder at 1630 cm^{-1} indicating the presence of water molecules in the complexes. The (N–H) stretching band of NO_2-BzH is not affected appreciably in its dihalo complexes indicating that NH nitrogen is not involved in bonding. The (C=N) stretch of the ligand is found at 1593 cm^{-1} which is observed at 1600±5 cm^{-1} in its complexes suggesting involvement of (C=N) nitrogen in bond formation[18]. Besides (C=N) strertch the ligand and its complexes display a number of bands in 6-16 μ region due to various modes of NO_2, (N–H), (C–N) and phenyl ring vibrations. The prominent bands of ligand and its complexes are observed at 1533±2, 1490±3, 1468±5, 1405±2, 1340±2, 1300±2, 1255±3, 1220±3, 1120±1, 1065±3, 950±10, 870±5, 830±1, 815±3, 755±1, 730±2, 670±2 and 640±5 cm^{-1}. The ir spectra of complexes could not be recorded in far ir region and nothing could be suggested about (M–N) vibrations.

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Complexes of Some Platinum Metals with 4-Amino-3,5-Dimercapto-1,2,4-Triazole

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IN a previous communication[1] the complexes of some bivalent metal ions with 4-amino-3,5-dimercapto-1,2,4-triazole (H_2AMT) were reported. It the present communication we are reporting the preparation and characteristion of complexes of Ru(II), Rh(III), Pd(II) and Pt(II) with H_2AMT.

Experimental

Preparation of complexes : $M(HAMT)_2$, ($M=Pd^{2+}$ or Pt^{2+}) : An aqueous ethanolic solution of metal chloride (1.0%, ~50 ml) was treated with pyridine dropwise to get a light yellow solution of $[M(Py)_4]Cl_2$. The resulting solution of tetrapyridino complex was refluxed on a steam bath with an excess of ligand (1 : 2.5 molar ratio) in ethanolic solution when almost insoluble precipitate of the *bis* chelated complex separated out. The product was collected on a filter, washed with ethanol and dried in air (yield almost quantitative).

$[Ru(HAMT)_2]$: An ethanolic solution of ruthenium(II) chloride[2] (1.0%, 50 ml) was refluxed with an excess of ligand (1 : 2.5 molar ratio) for half an hour when a dark green precipitate began to separate slowly. The product was filtered, washed with ethanol and dried in air. Yield about 70 – 80%.

$[Rh(HAMT)_2Cl.H_2O]$: An ethanolic solution of hydrated rhodium(III) chloride (2.0%, 50 ml) was refluxed with excess of ligand on a steam bath by adjusting *p*H to 2-3 with dilute hydrochloric acid for about 1 hr. The chloro complex $[Rh(HAMT)_2Cl.H_2O]$ separated as brick red precipitate. The product was collected on a filter, washed with ethanol and dried as usual.

$[Rh_2(AMT)_3]$: The complex was obtained as insoluble orange red precipitate, when an ethanolic solution of hydrated rhodium(III) chloride (*p*H 5-6) was refluxed with 1 : 2 molar ratio of ligand on a steam bath for about 1 hr.

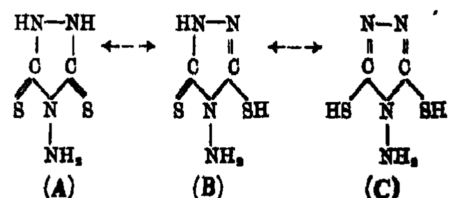
The ligand was prepared as reported earlier[1]. The platinum metal chlorides were obtained from Johnson and Mathey Ltd.

The analytical results and electronic reflectance or absorption bands of complexes with their tentative assignments are shown in Table 1.

Magnetic susceptibilities and electronic spectra of the complexes were measured as reported earlier[1]. Infrared spectra of the complexes were recorded in KBr disc on a Perkin Elmer 577 spectrophotometer.

Results and Discussion

The analytical results of complexes (Table 1) show that 4-amino-3,5-dimercapto-1,2,4-triazole (A) forms complexes with tautomeric forms B and C.



The attempt to prepare Ru(III) and Pt(IV) complexes was unsuccesful since they were reduced by the ligand to Ru(II) and Pt(II) respectively. The complexes of $HAMT^-$ as well as AMT^{2-} are almost soluble in ethanol and water but are sparingly soluble in DMF or dioxane. The poor solubility of the complexes indicates their polymeric nature. The complexes are diamagnetic, indicating four coordinated square planar structure for Pd(II) and Pt(II) while octahedral for Rh(III) and Ru(II) in these complexes. The solid reflectance spectrum of $Rh(HAMT)_2Cl.H_2O$ displays shoulders near 470 nm and 340 nm assignable to $^1A_{1g}\rightarrow{}^1T_{2g}$ and $^1A_{1g}\rightarrow{}^1T_{1g}+CT$ transitions (Table 1) in octahedral environment of rhodium(III) ions[3,4]. The reflectance spectrum of $Ru(HAMT)_2$ displays a broad and weak band near 570-580 nm assignable to $^1A_{1g}\rightarrow{}^1T_{2g}$ transition, similar to hexa-coordinated Ru(II) complexes[5,6]. The other d-d transition of Ru(II) complex could not be observed due to strong charge transfer absorption. In solid state $[Pd(HAMT)_2]$ shows a shoulder near 500 nm, while in solution it shows a number of bands between 350 and 200 nm (Table 1) attributable to ligand field and charge transfer bands[7]. Reflectance spectrum of $[Pt(HAMT)_2]$ displays a shoulder near 400 nm assignable to $^1A_{1g}\rightarrow{}^1B_{1g}$ transition[7] in square planar field.

The assignment of ir spectral bands of H_2AMT and its complexes has been reported previously[1]. In the present investigation it is found that NH_2 and NH stretching vibrations of the ligand in the complexes are not well resolved, rather it is observed as a broad and medium band near $3130\pm20\ cm^{-1}$. The NH_2 deformation vibrations (Table 2) of ligand are also shifted to higher frequencies suggesting the bonding of NH_2 nitrogen in these complexes. The thioamide bands (I to IV) of ligand are affected appreciably in complexes and are observed as broad and medium to weak bands in AMT^{2-} complexes, and as well resolved and

TABLE 1

Complex (colour)	%Metal Found (Calcd.)	%N Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)	Electronic band positions (nm)	Assignments
$Pd(HAMT)_2$	26.38	27.75	11.79	1.64	500	$^1A_{1g} \rightarrow {}^1B_{1g}$
(Deep red)	(26.55)	(27.95)	(11.98)	(1.49)	318*	$^1A_{1g} \rightarrow {}^1E_g$
					266	$^1A_{1g} \rightarrow {}^1B_{1u}$
					257	$^1A_{1g} \rightarrow {}^1A_{2u}$
					252	$^1A_{1g} \rightarrow {}^1E_u$
					208	$n \rightarrow \pi^*$
$Pt(HAMT)_2$	39 72	22.63	9.74	1.42	400	$^1A_{1g} \rightarrow {}^1B_{1g}$
(Dull yellow)	(39 86)	(22.88)	(9.81)	(1 22)		
$Ru(HAMT)_2$	25.10	28.07	12.20	2.35	570 sh	$^1A_{1g} \rightarrow {}^1T_{2g}$
(Deep green)	(25 43)	(28.18)	(12 09)	(2 01)	- 580	
$Rh(HAMT)_2Cl.H_2O$**	22.44	24 57	—	—	470 sh	$^1A_{1g} \rightarrow {}^1T_{2g}$
(Brick red)	(22.79)	(24.74)	—	—	340 sh	$^1A_{1g} \rightarrow {}^1T_{1g}$+CT
$Rh_2(AMT)_3$	31.56	25.84	11.20	1.75	465 sh	$^1A_{1g} \rightarrow {}^1T_{2g}$
(Orange red)	(31 65)	(25.83)	(11.08)	(1.84)		

* Absorption band in ethanol. ** Percent of halogen, Found. 7 53, Calcd. 7 83.

TABLE 2—IR BANDS IN cm^{-1}

H_2AMT	$[M(HAMT)_2]$ $H = Pd^{2+}, Pt^{2+}, Ru^{2+}$	$Rh_2(AMT)_3$	$Rh(HAMT)_2Cl.H_2O$	Assignments
—	—	—	3440 wb	ν(OH) of H_2O
3295 msp	3120±10 mb	3150 m	3140 mb	$\nu(NH_2)+\nu(NH)$
3110 —				
2650 sb	2980±5 wb	—	2940 sh	
2110 wb	—	—	—	ν(S-H)
1608 s	1620±10 m	1615 sb	1610 sh	$\delta(NH_2)+\delta(H_2O)$
			1585 sb	
1510 s	1520±5 m	—		
1472 sh	1485±5 m	1498 mb	1485 sb	Thioamide band I
1325 m	1390±10 mb	1400 sh	1390 sh	Thioamide band II
1255 sb	1270±5 m	1300 sb	1290 sb	$\beta(NH_2)$
1018 s	1060±10 w	1060 wb	1040 m	Thioamide band III
940 vs	980±5 w		980 sb	Thioamide band IV
			835 wb	(H_2O)
750 wb	740±10 w	748 m	720 mb	ν(C-S) contribution
725 ms	695±5 vs	675 mb	—	
645 s	620±5 s	620 wb	640 mb	Ring stretch
—	—	433 m	422 wb	ν(M-N) stretch
—	360±20 w	325 sh	335 w	ν(M-S) stretch

s=strong, m=medium, b=broad, w=weak, sh=shoulder, sp=sharp

medium to strong bands in $HAMT^-$ complexes. The thioamide band IV located at 940 cm^{-1} almost disappears in AMT^{2-} complexes but is observed with reduced intensity at 980±5 cm^{-1} in $HAMT^-$ complexes, indicating that one of the thione sulphur is free in monoanionic ligand. A weak band located at 750 cm^{-1} in free ligand attributable to ν(C-S) vibration is shifted to lower frequencies in all complexes. Thus it is inferred from the nature of shift of thioamide bands that one thioamide deprotonated thiol sulphur is coordinated in $HAMT^-$ while both the thioamide deprotonated thiol sulphur are bonded to AMT^{2-} complexes. A broad band at 835 cm^{-1} in the ir spectra of $[Rh(HAMT)_2Cl.H_2O]$ can be attributed to out of plane deformation vibration of coordinated water.

In far infrared region, a weak band (320-380 cm^{-1}) observed in a few complexes has been tentatively suggested to ν(M-S) vibration. The reduced intensity of ν(M-S) vibration is attributed to the polymeric nature of the complexes. The observed range of ν(M-S) vibration is well within the range of metal-sulphur stretching frequencies of S-bonded transition metal complexes with sulphur donor ligands[10,11].

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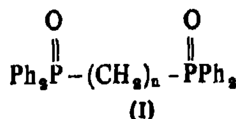
Donor Properties of Ditertiaryphosphine Dioxides towards Iron(III)

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COORDINATION chemistry of bifunctional organophosphorus ligands, namely, ditertiaryphosphine dioxides towards various metal ions has been reported[1]. However, there are known only two complexes with iron(III), viz., $[Fe(MBDPO)_3](ClO_4)_3$ and $[Fe(MBDPO)_3][FeCl_4]_3$ (MBDPO = 1,1-methylene*bis*(dibutylphosphine oxide). It was therefore considered worthwhile to study the coordination properties of bidentate ditertiaryphosphine dioxides (I) involving phenyl substituents on phosphorus towards iron(II) and iron(III).



The intention was to study the effect of ring size on stability and nature of complexes by increasing the number of methylene groups and using Mössbauer spectrometer as one of techniques for structure elucidation. In this communication, we are reporting complexes of 1,1-methylene*bis*(diphenylphosphine oxide) (MDPO), 1,2-dimethylene*bis*-(diphenylphosphine oxide) (EDPO), 1,4-tetramethylene*bis*(diphenylphosphine oxide) (BDPO) and 1,6-hexamethylene*bis*(diphenylphosphine oxide) (HDPO) with chloride, bromide, nitrate and perchlorate of iron(III). These have been characterised by elemental analysis, molar conductance, ir and reflectance spectra.

Experimental

The ligands MDPO, EDPO, BDPO and HDPO were prepared by oxidation of the corresponding ditertiaryphosphines with hydrogen peroxide (Lit. m.p. MDPO, 176-178°; EDPO, 256-58°; BDPO, 246-47° and HDPO, 196-97°)[2].

The complexes were prepared by the interaction of iron(III) salts with the ligands in suitable solvents. The solid products were obtained either on gentle heating or on subsequent treatment with petroleum ether (40-60°). Iron was estimated spectrophotometrically[3]. Carbon and hydrogen were analysed in University College of Sciences, Calcutta. The molar conductances of millimolar solutions of complexes in nitrobenzene were measured with Toshniwal Type CLOI/02A conductivity bridge. The ir spectra of the ligands and the complexes were recorded in the range 4600-650 cm^{-1} in nujol mulls using Spectromom-2000. The reflectance spectra of the complexes in the range

TABLE 1—THE ELEMENTAL ANALYSES AND SPECTRAL PROPERTIES OF COMPLEXES

Sl No.	Complex	Analysis %, Found, (Calcd) C	H	Fe	m p (°C)	ν(PO) cm^{-1}	λ_{max} nm
1	$FeCl_3MDPO$	50 80 (51 80)	4 39 (3 91)	10 43 (9 68)	268	1145 (s, sp) 1140 (w)	330 (m, sp), 480 (b, s), 520 (sh)
2	$FeCl_3BDPO$	55 53 (54 10)	5 08 (4 50)	8 82 (9 02)	212	1146 (s, sp) 1162 (s, sp)	360 (sh), 380 (s, sp), 400 (w)
3	$FeCl_3HDPO\,H_2O$	54 32 (54 01)	5 19 (5 10)	8 31 (8 40)	112	1139 (s, sp)	360 (sh), 380 (s, sp), 430 (s, sp), 400 (w)
4	$[Fe(MDPO)_3](ClO_4)_3\,H_2O$	54 58 (55.53)	3 90 (4 19)	3.75 (3 45)	300	1172 (m, sp)	350 (s, sp), 510 (w, b)
5.	$[Fe(EDPO)_2(ClO_4)][ClO_4]_2$	51.86 (50 62)	4 09 (4 05)	4 52 (4 54)	262	1138 (s, sp)	330 (sh), 360 (s, sp)
6	$[Fe(BDPO)(ac)_2(ClO_4)_2]ClO_4$	44 46 (43 90)	3 48 (3 60)	6 18 (6 89)	210(d)	1170 (s, sp)	350 (s, sp), 370 (sh)
7	$[Fe_2(MDPO)_3(NO_3)_4][NO_3]_2\,2H_2O$	50 14 (50 81)	4.65 (3 95)	6 52 (6.33)	221(d)	1154 (s, sp) 1170 (m, sp)	370 (sh), 390 (s, sp), 490 (w), 570 (w)
8.	$[Fe(EDPO)_2(NO_3)_2][NO_3].H_2O$	55 10 (55 71)	3 54 (4.46)	5 49 (5.00)	264	1140 (s, sp) 1170 (sh)	380 (s, sp), 430 (w), 460 (s, sp)
9	$Fe(NO_3)_3BDPO$	47 43 (48 00)	–	8 40 (8 00)	121	1134 (s, sp)	380 (s, sp), 430 (w), 460 (s, sp)
10.	$FeBr_3BDPO$	44.01 (44.50)	3 46 (3.60)	7.96 (7.42)	206	1139 (s, sp) 1150 (s, sp)	380 (sh), 420 (w), 490 (s, sp), 540(w)

d = decomposition, s = strong; m = medium, sp = sharp, sh = shoulder; w = weak, ac = acetone.
The ir spectra show the presence of lattice water in complexes.

300-700 nm were recorded with spectrophotometer VSU-2P.

Results and Discussion

The elemental analyses (Table 1) show the formation of complexes of stoichiometries; 1 : 1, 1 : 2, 2 : 3 and 1 : 3 (metal : ligand). The colours of complexes range from white to yellow to red. The melting points of complexes fall in the range of melting points of their respective ligands except those of HDPO. The molar conductance values of chloride complexes of MDPO, BDPO and HDPO indicate them to be essentially non-electrolytes (Λ 10.92, 15.95 and 15.32 ohm^{-1} cm^2 $mole^{-1}$, respectively). Similarly, the perchlorate complexes are formulated as, $[Fe(MDPO)_2](ClO_4)_3$, $[Fe(EDPO)_2ClO_4](ClO_4)_2$ and $[Fe(BDPO)(ClO_4)_2(ac)_2](ClO_4)$ (Λ 67.36, 56.36, 32.80 ohm^{-1} cm^2 $mole^{-1}$, respectively). The nitrate complex of MDPO is a 2 : 3 electrolyte and that of EDPO is a 1 : 1 electrolyte (Λ 48.01 and 20.40 ohm^{-1} cm^2 $mole^{-1}$, respectively) which are formulated as $[Fe_2(MDPO)_3(NO_3)_4](NO_3)_2$ and $[Fe(EDPO)_2(NO_3)_2](NO_3)$. However, the corresponding BDPO complex is a non-electrolyte (Λ 9.76 ohm^{-1} cm^2 $mole^{-1}$) and is analogous to complex of BDPO with iron(III) chloride.

The phosphoryl stretching frequencies in MDPO and EDPO appear as doublets at 1205, 1192 and 1190, 1180 cm^{-1}, respectively while in BDPO and HDPO as singlets at 1182, 1185 cm^{-1}, respectively (Table 1). The ν(PO) bands appear in the range 1172-1128 cm^{-1} in the complexes either as a singlet or a doublet. There is negative spectral shift of *ca* 22-52 cm^{-1} in $\nu(P=O)$ indicating that metal-ligand interaction takes place through phosphoryl group. The reflectance spectra is characteristic of iron(III) complexes[4-5] and λ_{max} falls in the range 330-645 nm (Table 1). Detailed studies on these as well as a number of related complexes are in progress.

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Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-Sulphaphenazole Complexes with La^{3+}, Y^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+}

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IN the present investigation, potentiometric studies have been carried out on 2-hydroxy-1-naphthalidene-sulphaphenazole and its complexes with some trivalent metal ions. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants (log K_1 and log K_2) of its metal chelates have been determined potentiometrically following the Calvin-Bjerrum pH-titration technique as adopted by Irving and Rossotti[1].

Experimental

The ligand 2-hydroxy-1-naphthalidene-sulphaphenazole was prepared by refluxing equimolar quantities of 2-hydroxy-1-napthaldehyde and the amine in alcohol-DMF mixture for about 2 hr. The crude product was repeatedly crystallised to obtain an analytically pure compound with m. p. 226°.

All the metal perchlorates used were prepared from metal salts and perchloric acid of A.R. Grade. These were standardised complexometrically by EDTA titrations[2].

Other experimental details were the same as in our earlier communication[3].

Results and Discussion

It may be mentioned that the ligand does not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the course of titration and by the absence of any significant drift in pH even after 2 hr. This was further confirmed by taking tlc of a sample titration mixture from time to time.

In the ligand, it is the phenolic-OH group which takes part in complex formation and the proton is replaced from it by the metal ion during chelation. As only one porton per ligand molecule is liberated, 'Y' the number of dissociable protons attached to each ligand molecule is one.

From the titration curves (Fig. 1), $\bar{n}_A$ values at various 'B' values (pH meter readings) were calculated and the formation curve (B vs $\bar{n}_A$) was plotted. The pK_1^H corresponding to phenolic H was obtained by half integral method at $\bar{n}_A=0.5$. This was further corroborated by plotting the graph of log $(\bar{n}_A/1-\bar{n}_A)$ vs B.

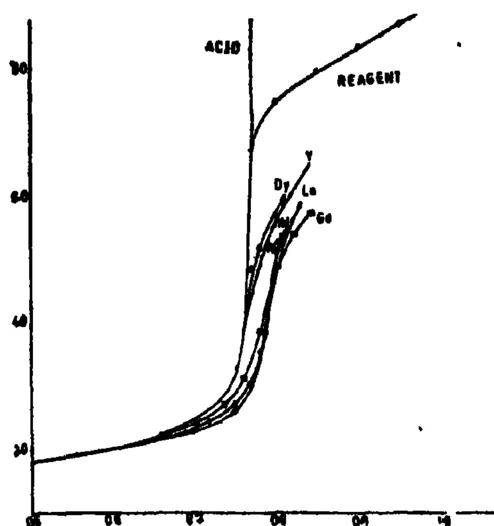


Fig 1. Titration curves of 2-hydroxy-1-naphthalidene-sulphaphenazole

From the titration curves, $\bar{n}$ and pL values for metal-ligand systems were also determined. From the curves ($\bar{n}$ vs pL) log K_1 and log K_2 values were determined by half integral method. In the cases of La^{3+}, Y^{3+}, Gd^{3+} complexes, the difference between log K_1 and log K_2 was found to be less than 1.78 log units; these were computed by least square method and are reported in Table 1.

TABLE—1

$t = 25°$ $\mu = 0.1M$

Cations	H^+	La^{3+}	Pr^{3+}	Nd^{3+}	Gd^{3+}	Dy^{3+}	Y^{3+}
log K_1	7 88	7.45	7 4	6 87	6 64	5 08	4.91
log K_2	–	4.52	–	4 80	4 61	–	4 61

The order of stability of metal chelates is found to be $La^{3+} > Pr^{3+} > Nd^{3+} > Gd^{3+} > Dy^{3+} > Y^{3+}$.

Acknowledgement

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A Potentiometric Study on the Complexes of Gadolinium, Erbium and Ytterbium in Aqueous Solution

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THE stability of complex ion or a molecule in a solution is determined by the nature of the central atom and the addends. The most important characteristics of the central atom determining the stability of the complex compounds are the degree of oxidation (the charge of the central ion in case of ionic complexes), the dimensions (ionic radii) and the electronic configuration. From this point of view rare earth metal ions form an interesting group which consist of similar electronic configuration and the trivial trivalent oxidation state. Thus, in the present study the effect of ionic radii and various ligands containing oxygen and nitrogen as donor atoms have been carried out. In previous publications some lower group of rare earth series have been studied[1-5]. In the present paper the rare earths under study are trivalent gadolinium, erbium and ytterbium using the following organic ligands:

i. 7-Iodo-8-hydroxyquinoline-5-sulphonic acid (IOSA)

ii. 8-Hydroxyquinoline-5-sulphonic acid (OSA)

iii. 1,2-Dihydroxybenzene (pyrocatechol, PYC)

iv. 2,3-Dihydroxynaphthalene-6-sulphonic acid (DHNSA)

v. 1,2-Dihydroxybenzene-3,5-disulphonic acid (Trivial name Tiron)

Experimental

Chemicals: All the chemicals used were of AnalaR Grade. Stock solutions (0.01 *M*) of IOSA, OSA, PYC (E.Merck); DHNSA, Tiron (Fluka, A.G.) were freshly prepared in double distilled carbon dioxide free water. The rare earth solutions were prepared by dissolving rare earth metal trioxide (Johnson and Matthey) in minimum quantity of perchloric acid and standardized by complexometric method[6].

Instruments: A pH meter (Toshniwal CAT No. CL-43 Type) with combined glass-calomel electrode assembly was used to obtain pH of solutions during the titration. Nitrogen gas was passed continuously during the course of titration. The titration cell was immersed in an electronically controlled thermostatic bath maintained at 35±0.1°. The contents of the cell were continuously stirred during the titration. The pH meter was calibrated against standard buffers.

Results and Discussion

Irving-Rossotti's *p*H titration technique[7] has been adopted for the evaluation of "proton-ligand" and "metal-ligand" stability constants at 35° and ionic strengh 0.2 *M* ($NaClO_4$). One or more of the following computational methods have been used to evaluate the stability constants: (a) interpolation at half $\bar{n}$ values, (b) linear extrapolation method, (c) elimination method and (d) mid-point method. Tables 1 and 2 give the values of proton-ligand and metal-ligand stability constants, respectively.

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS AT 35° AND μ=0.2 *M* ($NaClO_4$)

Ligand	$\log K_1^H$		$\log K_2^H$		$\log B^H$	
	A	B	A	B	A	B
IOSA	7 01	7 02	2 60	2 61	9.61	9 63
OSA	8 07	8 06	3 80	3 81	11.87	11 87
PYC	—	11 61(c)	9.05	9 08	20.69(b,c)	20.42(d)
DHNSA	—	11 40(c)	7 97	7.98	19.38(b,c)	19 4 (d)
Tiron	—	12 21(d)	7 59	7 59	19 8 (b,d)	19 8 (d)

TABLE 2—METAL-LIGAND STABILITY CONSTANTS AT 35° AND μ=0.2 *M* ($NaClO_4$)

Ligand (L)	$\log K_{Gd-L}$		$\log K_{Er-L}$		$\log K_{Yb-L}$	
	A	B	A	B	A	B
IOSA	6 07	6 08	6 13	6 13	6 33	6 35
OSA	6 56	6.60	6 64	6 65	6 86	6.86
PYC	9.60	9.57	–	9.87	—	10 28
DHNSA	10.10	10 13	10 18	10.17	10 46	10 49
Tiron	13.98	13.37	13 81	13.80	14 05	13.99

All the ligands under investigation are bidentate and form stable five membered rings during complexation. The order of stability constants in terms of the various ligands under study was found to follow the order IOSA < OSA < PYC < DHNSA < Tiron (Fig. 1). Both IOSA and OSA coordinate through phenoxide O atom and quinoline N atom.

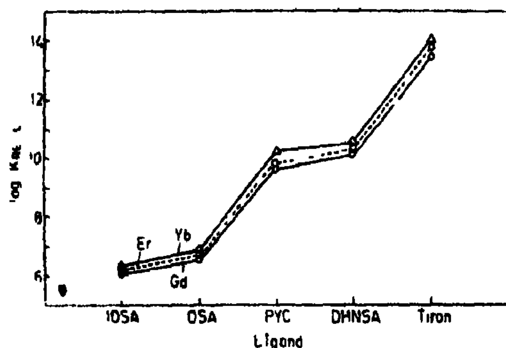


Fig. 1 Variation of stability constants of rare earths with various organic ligand

In case of PYC, DHNSA and Tiron, two phenoxide O atoms at *ortho* positions are acting as donor atoms. Thus, it is observed that in the above ligands, where two phenoxide O atoms are present, they form more stable complexes as compared to the ligands containing only one phenoxide O atom and one quinoline N atom as donors.

The donor atoms and chelating ring structure formed with the same metal ion are identical both in IOSA and OSA, but in the case of IOSA molecule, the presence of an electron withdrawing iodo group as compared to OSA (the iodo group decreases the basicity of IOSA compared to OSA) may result in lower stability. Such a trend has also been observed by Pujari and Munshi[8] in the case of yttrium chelates. Tiron has the highest stability which might be due to two sulphonate groups which increase the reactivity of phenoxide groups towards coordination[9-10]. DHNSA is next to Tiron and has higher stability as compared to PYC. This might be due to the presence of naphthalenering[10].

Fig. 2 shows the variation in the values of stability constant of rare earths with ionic radii. It has been observed that the value of the stability constants follow the trend Gd(III) < Er(III) < Yb(III) which is identical with the general trend shown by trivalent lanthanoids with majority of aminopolycarboxylic acids[11].

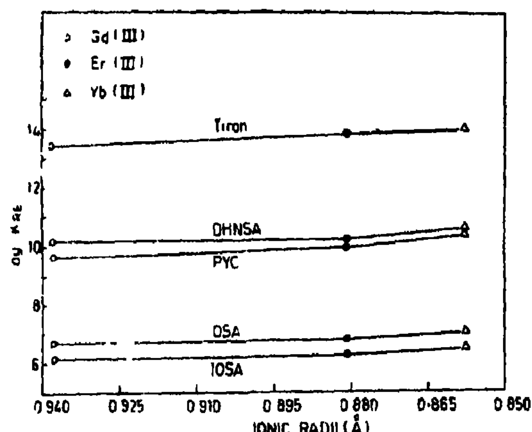


Fig 2. Variation of stability constants of rare earths with ionic radii

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Viscosity B Coefficient of Phenols and Benzyl Alcohol

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THE viscosity B coefficient of Jones-Dole's equation is known to be sensitive to the nature of solute-solvent interactions, i e. it is related to the modification of micro-viscosity of the solvent in the neighbourhood of the solute particle as compared to the bulk viscosity. A structure-making solute is expected to have a positive B coefficient in the given solvent whereas a structure-breaker may have a less positive or altogether negative B coefficient[1]. However, a large solute may always possess a positive B coefficient (irrespective of the nature of its interaction with the solvent) due to the "obstruction effect", i e., a bending of the solvent streamlines round a large solute particle. The sign and magnitude of the temperature coefficient, $\frac{dB}{dT}$, rather than B, therefore, often provides a better index of solute-solvent interactions. This observation is attributed to an increased thermal mobility of water molecules at higher temperatures which causes the structure-promotion by a solute more difficult (i.e., B is rendered less positive) so that $\frac{dB}{dT}$ becoms negative. A structure-breaker, on the other hand, exerts a less disruptive influence on the structure of the solvent (which is already broken) at an elevated temperature, and hence the corresponding $\frac{dB}{dT}$ is positive. These considerations are obviously independent of the size of the solute particle.

In the present study, viscosity B coefficient of phenol, resorcinol, *p*-cresol and benzyl alcohol has been determined in aqueous medium at temperatures 30, 35 and 40°. The magnitude and sign of $\frac{dB}{dT}$ at 35° is also ascertained for each solute. The B coefficients were obtained by having recourse to a graphical technique based on Jones-Dole's equation,

namely, $$\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \quad (1)$$

where η_0 and η are the respective viscosity coefficients, at the same temperature, of pure water and the solution of molar concentration C, while A and B are empirical constants, sensitive to solute-solute interactions (Grüneisen effect) and solute-solvent interactions.

A rearrangement of eq. (1) leads to

$$\frac{\frac{\eta}{\eta_0} - 1}{\sqrt{C}} = A + B\sqrt{C} \quad \dots (2)$$

so that a plot of $\frac{\frac{\eta}{\eta_0} - 1}{\sqrt{C}}$ vs $\sqrt{C}$ gives a stright line of slope B and intercept A.

An Ubbelhode type of viscometer with an average flow time of 502 sec for 10 ml of water (at 30°) was used for viscosity determinations. AnalaR grade materials, whenever available, have been used ; otherwise, the purest grade available has been further purified. The solutions were prepared in deionised water of conductivity less than 3 μ mho cm^{-1}. The temperatures of study have been kept constant within ± 0.05° by the use of a water thermostat provided with an electrical contact thermometer along with a solid-state relay unit.

The results have been entered in Table 1. That the B coefficient of phenol at lower temperatures (e.g. 30°) is higher than that of resorcinol, but lower than the value for *p*-cresol, is consistent with a corresponding change in the net content of hydrophobic (e.g. methyl) and hydrophilic (e.g. hydroxyl) groups in these compounds. An increase in the former (as in *p*-cresol) is expected to lead to an increase in the B coefficient in aqueous medium, due to structure-promotion in water through what is known as "hydrophobic hydration"[2]. Resorcinol, with a higher content of structure-breaking hydroxyl groups, has the lowest B (at 30°). Aliphatic compounds, belonging to a particular homologous series (e.g. the carboxylates), also exhibit a similar increase in B coefficient with the lengthening of the hydrophobic carbon chain[3]. However, the B values for phenols are found, on comparison with those for aliphatic carboxylates, surprisingly small for six-carbon solutes (intermediate between the values for two- and three-carbon carboxylates[3]) ; this low contribution of a phenyl group may have arisen from the inability of water molecules to accommodate themselves inside the benzene ring for spatial restrictions. Such a partial loss of structure-making (i.e. "ordering") influence of methylene groups, induced by "aromaticity", is in line with the general higher water-solubilities of aromatic compounds as compared to the open-chain analogues, having the same number of carbon atoms (i.e., due to a lower "negentropy" effect of the aromatic compounds on water structure).

A positive $\frac{dB}{dT}$ at 35° for resorcinol, whereas the negative values for phenol and *p*-cresol (the latter having it more negative), are also in agreement with the generalisations made in the introductory part. Consequent of these opposite signs of $\frac{dB}{dT}$, B of phenol, at a high enough temperature such as 40°, is rendered lower than that of resorcinol.

The B coefficient of benzyl alcohol, a molecular isomer of *p*-cresol, exhibits a somewhat erratic

TABLE—1

Viscosity of water (η_0) at 30° = 0.7975 cp, 35° = 0.7194 cp, 40° = 0.6529 cp

Density of water (ρ_0) at 30° = 0.9956 g cm^{-3}, 35° = 0.9940 g cm^{-3}, 40° = 0.9922 g cm^{-3}

Solution	Molar concentration/M (C)	Coefficient of viscosity of solution/cp, η at			B coefficient (slope of linear plot of $\frac{\eta-\eta_0}{\eta_0\sqrt{C}}$ vs $\sqrt{C}$) at			$\frac{dB}{dT}$ at 35°
		30°	35°	40°	30°	35°	40°	
	0.025	–	0.7255	0.6565				
	0.05	0.8104	0.7280	0.6592				
	0.08	0.8177	0.7311	0.6627				
Phenol	0.10	0.8228	0.7348	0.6664	0.230	0.218	0.192	−0.0037
	0.15	–	0.7432	0.6758				
	0.20	0.8434	–	–				
	0.30	0.8593	–	–				
	0.03	0.7994	–	–				
	0.05	0.8060	0.7288	0.6620				
	0.10	0.8140	0.7374	0.6706				
Resorcinol	0.15	–	0.7458	0.6786	0.189	0.216	0.244	+0.0054
	0.20	–	0.7538	0.6867				
	0.25	–	0.7625	0.6954				
	0.30	0.8508	–	–				
	0.50	0.8896	–	–				
	0.05	0.7956	0.7315	0.6632				
	0.075	0.8031	0.7380	0.6683				
p-cresol	0.10	0.8101	0.7432	0.6740	0.366	0.326	0.295	−0.0065
	0.12	0.8163	0.7484	0.6797				
	0.025	–	0.7244	0.6576				
	0.05	–	0.7296	0.6626				
	0.075	0.8140	0.7345	0.6670	0.322	0.272	0.260	–
Benzyl alcohol	0.10	0.8200	0.7397	0.6712				
	0.15	0.8309	0.7512	0.6816				
	0.20	0.8406	–	–				
	0.30	0.8629	–	–				

temperature-dependence (an increase in B with temperature followed by a small drop beyond 35°; the $\frac{dB}{dT}$ at 35° for benzyl alcohol is, therefore, not quoted in Table 1), eventhough the values are close to those for p-cresol. This perhaps results from a partial overlapping of the structure-making and structure-breaking spheres of influence of the hydrophobic methylene and hydrophilic hydroxy groups, situated in close proximity in the side-chain, $-CH_2OH$, in benzyl alcohol. This gets a qualitative support from similar observations reported for the enthalpy of transfer of methanol from water to heavy water (as compared to that for higher alcohols)[4], as well as the reported heats of transport of α-alanine and β-alanine in aqueous medium[5].

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The Reaction of Isatin with Active Methylene Group. Part—I : Formation of 5-(2-Oxo-3-indolinylidene)-3-Aryl-2,4-Thiazolidindiones—A New Class of Thioindigoid Dyes

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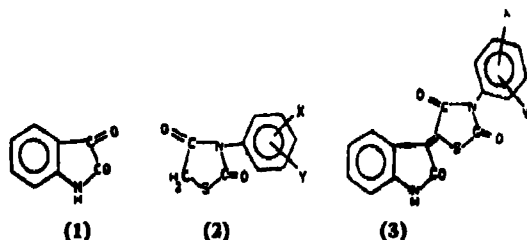
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THE methylene group of substances having the structure $-COCH_2NH-$ condenses readily with the carbonyl group of aldehydes and ketones[1]. Active methylene group present in the 4-thiazolidinone ring has also been found to react with aryldiazonium salts[2] and isatino carbonyl group[3].

A number of derivatives of isatin-β-thiosemicarbazone are reported to have antiviral activity[4]. Because of their usefulness and in order to examine the reactivity of the methylene group of 2,4-thiazolidindiones, we have undertaken the preparation of 5-(2-oxo-3-indolinylidene)-3-aryl-2,4-thiazolidindiones which form a new class of thioindigoid dyes.

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The synthesis of these thioindigoid dyes (3) and elucidation of their structures are reported in the present communication. 3-Aryl-2,4-thiazolidindiones (2), the starting materials, were prepared by the cyclization of symmetrical *bis*-arylthiocarbamides with 2-chloroacetic acid in glacial acetic acid medium. The nmr, ir and analytical data are consistent with the structures of these thiazolidindiones. They were further condensed with an equimolar quantity of isatin (1) in presence of fused sodium acetate in glacial acetic acid and acetic anhydride mixture forming the title compounds (3).



The assignment of structure of the dyes (3) was done on the basis of elemental analyses and ir spectral data.

The thioindigoid dyes formed different shades of orange to brick red crystals and dissolved in concentrated sulphuric acid producing deep orange coloured solutions.

Experimental

All melting points were taken in open capillary tubes on a Gallenkamp apparatus and are uncorrected. The element analyses (C, H and N) were carried out on a Coleman Analyser. The infrared spectra were recorded on a Perkin-Elmer 720 grating spectrophotometer as nujol mulls, while the nmr spectra were run on a Varian A60-D spectrometer at probe temperature of 44.5° as CCl_4 or deuterochloroform solutions using TMS as an internal standard.

Symmetrical bis-*(3-chloro-2-methyl)phenyl thiocarbamide* : This as well as other related symmetrical *bis*-arylthiocarbamides were prepared by the reaction of corresponding disubstituted anilines and carbon disulphide in presence of pyridine and iodine by the method of Fry[8] with slight modification that the reaction mixture was heated under reflux and this gave high yields.

3-(3'-Chloro-2'-methyl)phenyl-2,4-thiazolidindione : A mixture of symmetrical *bis*-(3-chloro-2-methyl)-phenyl thiocarbamide (3.2 g), monochloroacetic acid (1.0 g) and glacial acetic acid (10 ml) was refluxed on a water bath for 6 hr. The reaction mixture was allowed to cool, poured into cold water and filtered. The solid mass was washed with water and crystallised from ethanol to give 3-(3'-chloro-2'-methyl)phenyl-2, 4-thiazolidindione, yield 70%, m.p. 115°. Anal. Found : C, 49.56 ; H, 3.37 ; N, 5.62 ; S, 13.16. Calcd. for $C_{10}H_8ClNO_2S$; C, 49.69 ; H, 3.31 ; N, 5.80 ; S, 13.25%. IR (nujol) : 1760(m), 1700(s), 1590(m), 1518(m) cm^{-1}. NMR ($CDCl_3$) : δ 6.98 – 7.66 (m, 3H, ArH), 4.15 (s, 2H, CH_2), 2.20 (s, 3H, CH_3).

Similarly other 3-aryl-2,4-thiazolidindiones were prepared from reaction of different symmetrical *bis*-arylthiocarbamides and monochloroacetic acid in glacial acetic acid. Their yield, melting point, analytical and spectral data are reported in Table 1.

5-(2-Oxo-3-indolinylidene)-3-(5-chloro-2-methyl)-phenyl-2,4-thiazolidindione : A mixture of 3-(5-chloro-2-methyl)phenyl-2,4-thiazolidindione (0.72 g ; 3 mmole), isatin (0.51 g ; 3.5 mmole), anhydrous sodium acetate (1.0 g), acetic anhydride (1.0 ml) and glacial acetic acid (10 ml) was placed in a

TABLE 1—3-ARYL-2,4-THIAZOLIDINDIONES[a](2)

Sl. No.	Substituents X	Substituents Y	m.p. °C	Molecular Formula	%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	NMR Spectral data[b] δ_{SCH_2CO}	NMR Spectral data[b] δ_X	Characteristic IR bands (cm^{-1})
1.	2-CH_3	5-Cl	118	$C_{10}H_8ClNO_2S$	49.72 (49.69)	3.21 (3.31)	5.65 (5.80)	3.96 (s, 2H)	2.23 (s, 3H)	1750(m), 1680(s), 1575(m), 1515(m)
2.	2-CH_3	3-Cl	115	$C_{10}H_8ClNO_2S$	49 56 (49 69)	3.37 (3.31)	5.62 (5 80)	4.15 (s, 2H)	2.20 (s, 3H)	1760(m), 1700(s), 1590(m), 1518(m)
3.	4-CH_3	3-Cl	130	$C_{10}H_8ClNO_2S$	49 81 (49.69)	3.26 (3 31)	5.68 (5.80)	3.93 (s, 2H)	2 36 (s, 3H)	1760(m), 1680(s), 1580(m), 1510(m)
4.	2-Cl	3-Cl	125	$C_9H_5Cl_2NO_2S$	41.18 (41 22)	2.05 (1.91)	5.26 (5 34)	4.20 (s, 2H)	—	1750(m), 1685(s), 1570(m), 1520(m)
5	2-Cl	4-Cl	110	$C_9H_5Cl_2NO_2S$	41.25 (41.22)	1 87 (1.91)	5.22 (5.34)	4.19 (s, 2H)	—	1750(m), 1680(s), 1580(m), 1520(m)
6	2-Cl	5-Cl	127	$C_9H_5Cl_2NO_2S$	41.29 (41 22)	1.76 (1 91)	5.29 (5.34)	4 19 (s, 2H)	—	1760(m), 1685(s), 1595(m), 1515(m)
7.	2-OCH_3	5-Cl	155	$C_{10}H_8ClNO_3S$	46.57 (46.60)	2.98 (3.11)	5.41 (5.44)	4.13 (s, 2H)	3.83 (s, 3H)	1760(m), 1680(s), 1590(m), 1520(m)
8.	4-OCH_3	3-Cl	167	$C_{10}H_8ClNO_3S$	46.48 (46.60)	3.05 (3.11)	5.31 (5.44)	4 15 (s, 2H)	4.00 (s, 3H)	1760(m), 1680(s), 1590(m), 1515(m)

[a] Yields were in the range of 50-70%.

[b] Aromatic protons appear at δ6.85-7.75 ppm as a multiplet of 3H intensity.

TABLE 2—5-(2-OXO-3-INDOLINYLIDENE)-3-(DISUBSTITUTED)PHENYL-2,4-THIAZOLIDINDIONES[a](3)

Sl. No.	Substituents X	Substituents Y	m.p. °C	Colour and shape of crystals	Molecular Formula	%C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	Characteristic IR bands (cm^{-1})
	2-CH_3	5-Cl	277-79	Orange, small needles	$C_{18}H_{11}ClN_2O_3S$	58.48 (58.32)	3.41 (3.00)	7.72 (7 55)	3200(w), 1745(m), 1685(s), 1615(m)
2.	2-CH_3	3-Cl	284-86	Bright orange, crystals	$C_{18}H_{11}ClN_2O_3S$	58.15 (58.32)	3 30 (3.00)	7.65 (7 55)	3275(w), 1750(m), 1690(s), 1645(s), 1620(s)
3.	4-CH_3	3-Cl	>310 dec.	Orange, fine crystals	$C_{18}H_{11}ClN_2O_3S$	58 60 (58.32)	2.92 (3.00)	7.85 (7 55)	3215(w), 1740(m), 1675(s), 1655(s), 1615(m)
4.	2-Cl	3-Cl	323-25	Brick red, microcrystals	$C_{17}H_8Cl_2N_2O_3S$	52.01 (52.19)	2.29 (2.06)	6 93 (7.16)	3400(m), 1745(m), 1690(s), 1620(m)
5.	2-Cl	4-Cl	161-62[b]	Orange yellow, powder	$C_{17}H_8Cl_2N_2O_3S$	51.86 (52 19)	1.93 (2 06)	7.18 (7 16)	3300(w), 1740(m), 1700(m), 1645(s), 1620(m)
6.	2-Cl	5-Cl	266-68	Orange red, fine crystals	$C_{17}H_8Cl_2N_2O_3S$	51.90 (52.19)	2.23 (2.06)	7.40 (7.16)	3450(br,w), 1740(m), 1690(m), 1640(s), 1615(s)
7.	2-OCH_3	5-Cl	275-76	Bright orange, long needles	$C_{18}H_{11}ClN_2O_4S$	55.85 (55.90)	2 91 (2.86)	6.96 (7.24)	3400(br,w), 1745(m), 1685(s), 1615(w)
8.	4-OCH_3	3-Cl	330-33	Deep orange, fine crystals	$C_{18}H_{11}ClN_2O_4S$	56.18 (55.90)	3 05 (2.86)	7.02 (7.24)	3200(w), 1740(m), 1675(s), 1615(m)

[a] Yields were in the range of 80-95%.
[b] Shrinks at 130°.

round bottom flask. The flask was immersed in an oil bath preheated to 150-160°. The reaction mixture became orange at this temperature and within 10 min orange crystals began to appear. Heating under reflux was continued for 3 hr. It was then cooled and treated with excess of hot water. The thioindigoid dye was filtered and washed successively with hot water, dilute acetic acid and finally with ethanol. Recrystallization from ethanol afforded orange needles, yield 90%, m.p. 277-79°. Anal. Found : C, 58.43 ; H, 3.41 ; N, 7.72. Calcd. for $C_{18}H_{11}ClN_2O_3S$; C, 58.32 ; H, 2.99 ; N, 7.55%. IR (nujol) : 3200 (w, N-H stretch), 1745 (m, C=O stretch), 1685 (s, C=O stretch), 1615 (m) cm^{-1}

The general procedure exemplified above was employed for synthesis of all the thioindigoid dyes. Their properties and characteristic ir spectral bands are reported in Table 2.

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Reaction of Ninhydrin with Aromatic Amines and Ureas

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THE reactions of ninhydrin (I) with aromatic amines were studied by a number of workers[1-4]. Several reports are available on the reactions of ninhydrin with ureas[5-7]. The objective of our present investigation was to have some qualitative idea about the reactivity of ninhydrin towards nucleophilic addition using poor organic nitrogen nucleophiles and to prepare various conjugated systems from these reactions. In continuation of our previous studies[8-10] on the reactions of ninhydrin, we report here the syntheses of compounds (II)-(VII). These compounds appear to be new and are not reported in the literature.

Structures were assigned to these compounds on the basis of their nitrogen content, ir spectral data (Table 1) and formation of derivatives. 2,4-DNP did not react with the second carbonyl group of the mentioned compounds probably due to steric hindrance[9,10]. Compounds (II) and (IV) gave positive Lucas test indicating the presence of tertiary-OH groups. It is not clear why the adduct (II) in the case of α-naphthylamine did not undergo dehydration while the condensation product (III) was obtained in the case of β-naphthylamine. One probable explanation may be that the steric interaction due to the naphthalene ring becomes sufficiently strong to prevent the formation of the planar structure for the condensation

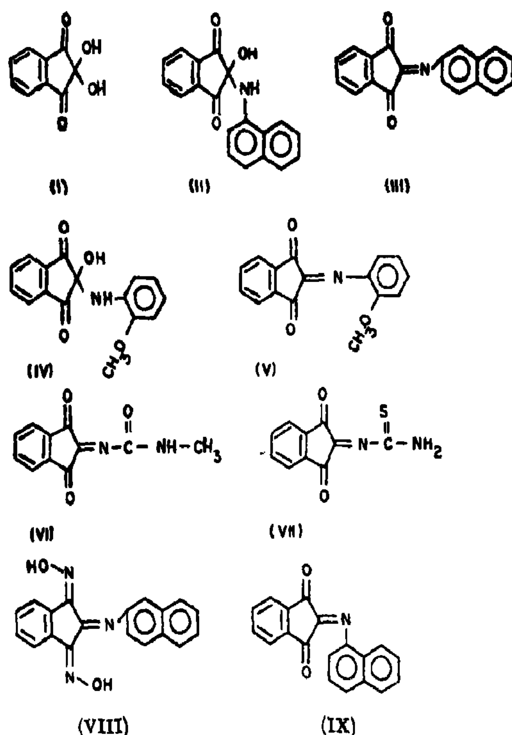


TABLE 1—IR ABSORPTION BANDS (in cm^{-1}) OF COMPOUNDS (II-VII)

(II)	3600 (b), 3400 (b) (OH, NH), 1690 (C=O), 1605 and 1570 (aromatic)
(III)	1760 and 1700 (C=O), 1630 (C=N), 1580 and 1525 (aromatic)
(IV)	3500 (b), 3400 (b) (OH, NH), 1710 (C=O), 1620 and 1590 (aromatic)
(V)	1710 (C=O), 1620 (C=N), 1600 and 1650 (aromatic)
(VI)	3320 (b), (NH), 1725 and 1690 (C=O), 1670 (C=N), 1600 and 1580 (aromatic)
(VII)	3600, 3300 and 3200 (b) (NH), 1725 (C=O), 1600 (C=N), 1590 and 1575 (aromatic), 1460 and 1450 (C=S)

product (IX). Unlike *p*-aminophenol and *p*-phenylenediamine[a] the addition product (IV), formed in the case of *o*-anisidine, was not dehydrated completely under the conditions used to give (V), possibly due to less resonance stabilization of the *o*-quinonoid structure than the *para* structure. Compounds (VI) and (VII) gained stability due to conjugation as a result of which the nucleophilicity of the amido nitrogen decreased and no further reaction took place. No reaction of ninhydrin was observed with 2,3-diaminotoluene, *o*-chloroaniline and *m*-nitroaniline in aqueous medium even at the refluxing temperature and using dilute H_2SO_4 as the catalyst. Inertness of these compounds may be due to a decrease in the electron availability of the amino nitrogen, primarily due to the steric effect, in the case of 2,3-diaminotoluene and -I effect due to Cl and $-NO_2$ group in the case of *o*-chloroaniline and *m*-nitroaniline, respectively.

Experimental

The formation of products from the various reactions was followed by tlc on silica gel plates using benzene-ethyl acetate (80 : 20) for α- and β-naphthylamines, methylurea and thiourea ; benzene-chloroform (90 . 10) for *o*-anisidine, 2,3-diaminotoluene and *o*-chloroaniline ; benzene-methanol (95 : 5) in the case of *m*-nitroaniline. The ir spectra were run as nujol mulls, except in the cases of (IV) and (V) where the spectra were run in $CHCl_3$, using an Unicam SP 1025 spectrophotometer. All the reactions were conducted in a manner analogous to the reaction of α-naphthylamine.

Reaction of ninhydrin with α-naphthylamine. Formation of 2-hydroxy-2-N-(α-naphthylamino)-1,3-indandione (II). Ninhydrin (1.78 g ; 0.01 mole) in water (50 ml) was added slowly to α-naphthylamine (1.42 g ; 0.01 mole) in water (50 ml). The mixture was stirred at room temperature (24°) for 76 hr. The yellow precipitate formed was filtered off, washed thoroughly with water, dried under vacuum, recrystallised from ethanol, and obtained as (II), m.p. 283-284°, yield 73% (Found : N,4.12. Calcd. for $C_{19}H_{13}O_3N$, N, 4 62%). The 2,4-DNP derivative crystallised from ethanol, m.p 296-298° (Found : N, 14 25. Calcd. for $C_{25}H_{17}O_6N_5$; N, 14.49%).

Reaction of ninhydrin with β-naphthylamine. Formation of 1,3-diketohydrindylidene-2-β-naphthylamine (III) : A yellow coloured product (III) was obtained which was recrystallised from ethanol, m.p. 225-227 , yield 62% (Found : N, 4.47. Calcd. for $C_{19}H_{11}O_2N$, N, 4.91%). The oxime derivative crystallised from ethanol, m.p. 168-170° (Found : N, 12.68. Calcd. for $C_{19}H_{13}O_2N_3$, N, 13.33%).

Reaction of ninhydrin with o*-anisidine. Formation of 2-hydroxy-2-N- (*o*-methoxyphenylamino)-1,3-indandione (IV) and 1,3-diketohydrindylidene-2-*o*-methoxyphenylamine (V)* . The reaction mixture was stirred for 57 hr. A brown coloured product was obtained, m.p. 80-82° (decomp.), which showed five spots in tlc, two of which corresponded to *o*-anisidine and ninhydrin. The product was purified by preparative tlc and two products (IV) and (V) were isolated, yields 25% and 40%, respectively. Compound (IV), R_f value 0.41, m.p. 86-88° (Found : N, 4.63. Calcd. for $C_{16}H_{13}O_4N$; N, 4.94%). The 2,4-DNP derivative had m.p. 102-104° (Found : N, 14.87. Calcd. for $C_{22}H_{17}O_7N_5$; N, 15.11%). Compound (V), R_f value 0.81, m p. 90-92° (Found : N. 4.97. Calcd. for $C_{16}H_{11}O_3N$; N, 5.28%). The 2,4-DNP derivative had m.p. 143-145° (Found : N, 15.10. Calcd. for $C_{22}H_{15}O_6N_5$; N, 15.73%).

Reaction of ninhydrin with methylurea. Formation of 1,3-diketohydrindylidene-2-N-methylcarbamide (VI): The reaction mixture was stirred for 105 hr. A white solid was isolated as (VI) which was recrystallised from ethanol, m.p. 249-250°, yield 60% (Found : N, 12.62. Calcd. for $C_{11}H_8O_3N_2$; N, 12.96%). The 2,4-DNP derivative crystallised from ethanol, m.p. 268-269° (Found : N, 20.91.

Calcd. for $C_{19}H_{12}O_{6}N_{6}$; N, 21.21%). Its ir spectrum showed bands at 3280 (NH), 1690 (C=O), 1620 (C=N), 1610 and 1590 (phenyl), 1375 and 1336 (NO_2) cm^{-1}.

Reaction of ninhydrin with thiourea. Formation of 1,3-diketohydrindylidene-2-thiocarbamide (*VII*) *:* The reaction mixture was stirred for 70 hr. A white precipitate obtained as (VII) was recrystallised from ethanol, m.p. 228-229°, yield 64.5% (Found : N, 12.40 ; S, 15.02. Calcd. for $C_{10}H_{6}O_{2}N_{2}S$; N, 12.84 ; S, 14.67%). The 2,4-DNP derivative crystallised from ethanol, m.p. 247-249° (Found : N, 20.62 ; S, 7.76. Calcd. for $C_{16}H_{10}O_{5}N_{6}S$; N, 21.10 ; S, 8.04%).

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Potential Antithyroid Agents. Part-II : Synthetic and Pharmacological Studies on Some N-Aryl-N′-2(benzimidazolyl) thiocarbamides and N-aryl-N′-benzenesulphonylthiocarbamides

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THE antithyroid agents lower the metabolic rate by interfering with the synthesis, release or peripheral action of the thyroid hormone. Highly active antithyroid substances contain thiourea moieties, -NHCSNH-, capable of being easily oxidized and it has been suggested that the interference with thyroxine synthesis is by direct reaction between I_2 and SH (formed by enolization) to form a disulphide[1-4].

The present communication deals with the synthesis and pharmacological studies of some N-aryl-N′-2(benzimidazolyl) thiocarbamides and N-aryl-N′-benzenesulphonylthiocarbamides. The active antithyroid drug is carbimazole consisting of an imidazole nucleus. Therefore, it was of interest to prepare some benzimidazolyl thiocarbamides consisting of a benzimidazole nucleus alongwith an extra thioureylene group, by the action of arylisothiocyanates with 2-aminobenzimidazole. The interest in the synthesis and pharmacological studies of benzenesulphonylthiocarbamides as antithyroid drug is due to the fact that these compounds contain an extra sulphonamide grouping alongwith the thioureylene linkages. The synthesis has been effected by the condensation of benzenesulphonylisothiocyanate with appropriate aromatic amines.

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Experimental

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. IR spectra were obtained using KBr pellets and a Perkin-Elmer 720 Infracord spectrophotometer ; bands reported were at least of medium intensity. Elemental analyses were in good agreement with the theoretical values.

Arylisothiocyanates : These have been prepared according to the method reported in the literature[5].

Benzenesulphonylisothiocyanate : It has been synthesised by the method of McFarland and Houser[6].

N-Phenyl-N′-2(benzimidazolyl) thiocarbamide · A mixture of phenylisothiocyanate (2.7 g ; 0.02 mole) and 2-aminobenzimidazole (2.66 g ; 0.02 mole) in dry benzene (25 ml) was refluxed for 2 hr. After the reaction, the excess benzene was distilled off and the residue was washed with petroleum ether (40-60°) and finally with ether to remove any unreacted constituents. N-Phenyl-N′-2(benzimidazolyl) thiocarbamide thus formed was recrystallised from ethanol. It could be desulphured with alkaline plumbite solution, yield 4.2 g, 80% ; m.p. 110°. Anal. Found : C, 62.62 ; H, 4.38 ; N, 20.82 ; S, 11.90. Calcd. for $C_{14}H_{12}N_{4}S$; C, 62.68 ; H, 4.47 ; N, 20.89 ; S, 11.94%.

Other N-aryl-N′-2(benzimidazolyl) thiocarbmides were prepared similarly by the condensation of 2-aminobenzimidazole with different arylisothiocyanates.

The various N-aryl-N′-2(benzimidazolyl) thiocarbamides were characterised by elemental analyses. Presence of characteristic bands of N=C=S (1520 cm^{-1}) and substituted benzene ring (780 cm^{-1}) in the ir spectra of these compounds provided further confirmation of their molecular structure.

N-Phenyl-N′-benzenesulphonylthiocarbamide : A solution of aniline (1.86 g ; 0.02 mole) in benzene (20 ml) was gradually added to a solution of benzenesulphonylisothiocyanate (3.98 g ; 0.02 mole) in benzene (20 ml). After few min a white precipitate of N-phenyl-N′-benzenesulphonylthiocarbamide was formed, which was collected and washed with benzene, petroleum ether (40-60°) and finally with

TABLE 1—SYNTHETIC AND PHARMACOLOGICAL SCREENING RESULTS OF N-ARYL-N'-2(BENZIMIDAZOLYL) THIOCARBAMIDES AND N-ARYL-N'-BENZENESULPHONYLTHIOCARBAMIDES AS ANTITHYROID DRUGS IN INTACT RATS

R^1–NH–C(=S)–NH–C_6H_4–R

No.	Compound R^1	Compound R	Yield %	m.p °C	Thyroid radioactivity (dpm ± standard error) ^{131}I uptake	Thyroid radioactivity (dpm ± standard error) $PB^{131}I$	Inorganic ^{131}I	Approximate estimated activity in rats (thiouracil = 1.0)
1.	2-benzimidazolyl	H	80	110	3662±12	2842±15	738±32	>1
2.	-do-	2-CH_3	72	150	3546±42	2985±25	510±14	>1
3.	-do-	3-CH_3	70	78	3682±40	2781±15	886±28	>1
4.	-do-	4-CH_3	74	65	3487±50	3033±22	480±14	>1
5.	-do-	2-OCH_3	75	70	4234±38	3679±13	590±16	≥1
6.	-do-	4-OCH_3	78	80	4386±24	3812±18	526±11	≤1
7.	-do-	2-Cl	74	60	3165±22	2517±12	619±15	>1
8.	-do-	3-Cl	72	80	3286±30	2452±14	802±24	>1
9.	-do-	4-Cl	75	155	3182±24	2367±24	714±17	>1
10.	-do-	4-OC_2H_5	78	130	3614±15	2987±26	655±16	>1
11.	$C_6H_5SO_2$	H	90	120	5522±19	4897±23	587±12	<1
12	-do-	2-CH_3	85	180	5781±15	5126±10	578±14	<1
13.	-do-	3-CH_3	80	140	5653±18	5120±17	506±19	<1
14.	-do-	4-CH_3	82	124	5613±12	4976±20	612±14	<1
15.	-do-	2-OCH_3	78	122	4602±25	4123±12	465±18	<1
16.	-do-	4-OCH_3	76	132	4598±16	3976±14	592±13	<1
17.	-do-	2-Cl	68	130	4427±12	3792±18	603±11	≥1
18.	-do-	3-Cl	70	136	4398±20	3688±16	678±24	>1
19	-do-	4-Cl	74	125	4265±14	3661±13	569±21	>1
20.	-do-	4-OC_2H_5	72	102	5836±24	5189±11	620±15	<1
21.		Control (Blank)			8478±50	7196±42	1238±28	
22.		Thiouracil			4463±62	3822±30	620±18	1.0

* Concentrations of test compounds equimolar to thiouracil, the analytical results for C, H, N and S in these compounds agreed with ±0.5% of the theoretical values

ether to remove any unreacted constituents. The thiocarbamide thus obtained was recrystallized from ethanol, and could be desulphured with alkaline plumbite solution, yield 5.75 g, 90%; m.p. 120°. Anal. Found: C, 53.30; H, 4.02; N, 9.52; S, 21.88. Calcd. for $C_{13}H_{12}N_2O_2S_2$; C, 53.42; H, 4.10; N, 9.58; S, 21.91%.

Similarly, other N-aryl-N'-benzenesulphonylthiocarbamides were prepared by condensing benzenesulphonylisothiocyanate with different amines and they are listed in Table 1.

Analytical results and ir spectra form the basis of the structure of the compounds. The ir spectra (KBr) show characteristic bands in the region 1350 cm^{-1}, 1510 cm^{-1} and 760 cm^{-1} indicating the presence of sulphonamido group, thioureido linkage and substituted benzene ring.

Pharmacological screening (7-11): Male Sprague-Dawley rats (100-125 g) were maintained on a low-iodide diet for 3 days, then divided into groups of four rats each. The animals in each group received an intraperitoneal injection of 1 ml of either a blank (0.9% NaCl), thiouracil or one of the test compounds. One hour after the administration of 1 μ Cu of $Na^{131}I$, the animals were sacrificed and the thyroids removed. The whole lobes were placed in ground glass homogenizing tubes and counted in a Nuclear-Chicago well scintillation counter to determine total iodide uptake. The whole lobes were then homogenized in 1 ml of 0.05 *M* barbital buffer (*p*H 8.6) containing $1.0\times10^{-4}M$ thiouracil. 1 ml of cold 20% trichloroacetic acid (TCA) was added and the homogenate centrifuged. The precipitate was washed twice with 1.0 ml of cold 10% TCA. The original supernatant liquid and the two washings were combined and the radioactivity was determined. The ^{131}I in this fraction indicated inorganic ^{131}I or TCA soluble ^{131}I. The washed precipitate was counted in the homoganising tube. The radioactivity in this fraction indicated the $PB^{131}I$ (protein-bound iodine) or the TCA precipitable ^{131}I. The counts were all corrected for counting efficiency and are expressed as disintegrations per minute.

All compounds were dissolved in saline for injection. Thiouracil was dissolved with heating to 55°. Compounds nos. 10 and 20 were only partially soluble in saline, EtOH or NH_4OH and therefore they were injected as a suspension in saline. All compounds were assayed at concentrations equimolar and ten times equimolar to 0.5 mg of

thiouracil (3.9 μ moles) and the biological effect was almost the same at both the doses. Table 1 summarizes the results of screening observations.

All compounds have antithyroid effects upto some extent and appear to inhibit incorporation of I_2 in a manner similar to thiouracil. Compounds nos. 2-5, 7-10 and 17-19 appear to be slightly more potent than thiouracil.

Mode of action and effect of substituents on antithyroid activity : The thioureylene linkage in these compounds is capable of forming an -SH grouping by enolisation. The suggestion has been made that the interference with thyroxine synthesis was by a direct reaction between iodine and sulphydryl grouping to form a disulphide[1*]. Since this reaction proceeded at a rate considerably faster than the iodination of tyrosyl group, the competition could be quite favourable for diversion of iodine away from organic binding.

These data suggest that a disulphide bond in thyroid tissue is cleaved by antithyroid compounds containing thioureylene linkage to form a new disulphide bond. This formulation is supported by chemical studies in which thiourea was found to cleave the disulphide bond of cystine to yield the mixed disulphide S-guanylthio-l-cysteine[18].

It is evident from the results of pharmacological studies that the introduction of chloro group in benzene ring enhances the activity to some extent.

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Chemical Investigation of *Wrightia mollissima*

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WRIGHTIA (fam. Apocyanaceae) is a genus o shrubs and small trees distributed in tropica Africa, Asia and Australia[1]. The genus owe it importance both from its economic and medicina points of view. The medicinal properties o *W. mollissima* are similar to *W. tinctoria* anc *Holarrhena antidysenterica*, whose bark is usec medicinally as a drug in amoebic dysentry Survey of literature reveals that no work has beer done previously on this plant. Hence a chemica investigation of its stem and leaves was undertaken We have isolated α-amyrin acetate, taraxerol acetate lupenone, taraxerol and β-sitosterol from petroleur ether extract while no crystalline compound coulc be isolated from ethanolic extract.

Finely powdered stem and leaves were extractec with petroleum ether (60°-80°) in soxhlet apparatu followed by extraction with ethanol.

Petroleum ether extract · It was concentratec under reduced pressure to a semi solid mass, whicl was chromatographed over silica gel.

α-Amyrin acetate Elution of column witl hexane and benzene (3 : 1) yield α-amyrin acetat as white crystalline compound (chloroform methanol), m p. 225°-6°. Alkaline hydrolysis yieldec α-amyrin, m.p 194°-5°. Identical (m.m.p., tlc anc ir) with authentic sample.

Taraxerol acetate : Elution of the column witl hexane-benzene (1 : 1) furnished white needle (chloroform) of taraxerol acetate, m.p. 295°-7° Alkaline hydrolysis gave taraxerol, m.p. 282°-3° Identity confirmed by comparison (m.m p., tlc anc ir) with authentic sample.

Lupenone : Further elution of the column witl benzene gave lupenone as white crystals (ether) m.p. 170°-1°, $NaBH_4$ reduction gave lupeol, m.p 215°. Identical (m.m.p., tlc and ir) with authenti sample.

Taraxerol · Elution of the column with benzen also yielded taraxerol as fine needles (chloroform methanol), m.p. 282°-3°, acetate (Ac_2O/Pyr), m.p 295°. Finally confirmed by comparison (m.m.p. tlc and ir) with authentic sample.

β-Sitosterol : Elution of the column witl benzene-ethylacetate (98 : 2) furnished whit crystals (chloroform-methanol) of β-sitosterol, m.p 135°-7°, acetate (Ac_2O/pyr), m.p. 128°. Identica (m.m.p., tlc and ir) with authentic sample.

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Alcoholic extract : Column chromatography of ethanolic extract over silica gel did not yield any crystalline compound.

Acknowledgement

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Reference

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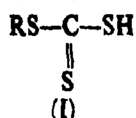
Mercurimetric Determination of Organotrithiocarbonates and A Method for the Analysis of Mercaptans

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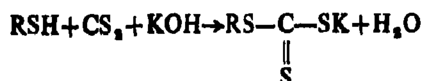
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ORGANOTRITHIOCARBONATES are the salts of the corresponding trithiocarbonic acids (I) and

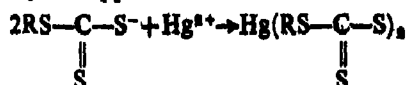


are prepared through the reaction of mercaptans with carbon disulphide in the presence of an alkali :



They find applications[1] as flotation agents, vulcanisation accelerators, pesticides, plant defoliants, rust inhibitors, lubricating oil additives and modifiers in bulk styrene polymerisation. Some trithiocarbonates have recently been reported to possess activity as anti radiation drugs. Inspite of their numerous applications in industry, agriculture and medicine, their determination has not received much attention. Verma and Kumar[2–5] recently described some oxidimetric methods for the determination of these compounds in aqueous and non-aqueous media.

The fact that organotrithiocarbonates react with mercury and other heavy metals to form salts, is already known [1,8,9]. The present communication reports a method for the determination of organotrithiocarbonates based on their tendency to react with metals to form salts. The use of mercury(II) is described for the first time for the determination of these compounds. Diphenylcarbazide has been found a suitable indicator. The end-point is marked by the appearance of blue colour.



The simplicity and reliability of the above method prompted us to apply this method to the determination of mercaptans after their transformation to the corresponding organotrithiocarbonates through reaction with carbon disulphide in presence of alkali. The transformation has been found to be extremely fast and quantitative[6,7]. Though mercury(II) salts have been used for the direct determination of mercaptans, doubts have frequently been expressed over the uniform stoichiometry of the reaction, that is, one or two molecules of mercaptans could react forming both RSHgX and $(RS)_2Hg$ compounds[10,11]. These observations in fact lead to the use of organomercury compounds (containing only one available mercury valency) in place of mercury(II) salts. The proposed method involving the transformation of mercaptans to organotrithiocarbonates is free from such ambiguity since the stoichiometry of the reaction of mercury(II) with organotrithiocarbonates is clear.

The proposed methods for the determination of organotrithiocarbonates and mercaptans are simple, rapid, accurate and reliable. They possess wide applicability.

Experimental

Mercury(II) acetate, 0.0125 M *in water :* The solution was standardised as described by Vogel[12].

Organotrithiocarbonates : The compounds were prepared and purified as described earlier[1,8]. The purity of the compounds was checked by iodimetric titrations[8].

Mercaptans : Isopropyl-, isobutyl-, benzyl- and dodecyl mercaptans as well as β-mercaptoethanol and thiophenol were distilled before use. 2-Mercaptobenzothiazol was used as received.

Diphenylcarbazide : 0.1% solution in ethanol.

Procedure :

(*a*) *Determination of organotrithiocarbonates :* Aliquots of the solution in water of each trithiocarbonate were taken in titration flasks and diluted with 40 ml of water. Each solution was mixed with 0.5 ml of diphenylcarbazide indicator and titrated at room temperature (24°) with standard (0.0125 *M*) mercury(II) acetate solution. The end-point was marked by the appearance of blue colour. From the volume of standard mercury(II) acetate solution used corresponding to the end-point in each titration, the amount of each trithiocarbonate was calculated. Results are given in Table 1.

(b) *Determination of mercaptans :* To aliquots (1-5 ml) of solutions in acetonitrile of each mercaptan were added another 5 ml of acetonitrile,

TABLE 1—MERCURIMETRIC DETERMINATION OF ORGANOTRITHIOCARBONATES AND MERCAPTANS (THROUGH TRITHIOCARBONATE FORMATION)

Compounds	Values are mean of ten determinations with standard deviation (±) Amount found*, mg	Amount found**, mg
Organotrithiocarbonates (TTC) RS—C(=S)—SK		
Benzyl TTC (R, $C_6H_5CH_2$-)	5.05, 0.063	12.10, 0.080
Dodecyl TTC (R, $C_{12}H_{25}$-)	5.04, 0.048	11.90, 0.098
β-Ethanol TTC (R, $OHCH_2CH_2$-)	4.96, 0.061	12.09, 0.080
Isopropyl TTC [R, $(CH_3)_2CH$-]	5.00, 0.052	12.07, 0.101
Isobutyl TTC [R, $(CH_3)_2CH\ CH_2$-]	4.95, 0.078	11.98, 0.089

* Amount taken, 5 mg, ** Amount taken, 12 mg

Mercaptans		
Benzyl mercaptan	4.03, 0.056	10.00, 0.076
Dodecyl mercaptan	4.00, 0.062	10.08, 0.101
β-Mercaptoethanol	3.98, 0.048	9.92, 0.092
Isobutyl mercaptan	4.00, 0.058	10.10, 0.085
Isopropyl mercaptan	3.96, 0.079	9.98, 0.080
Thiophenol	4.03, 0.088	10.03, 0.102
2-Mercaptobenzothiazol	4.05, 0.086	9.91, 0.084

* Amount taken, 4 mg, ** Amount taken, 10 mg

0.5 ml of carbon disulphide, 5-7 ml of potassium hydroxide (approx. 0.05 *N*) and 30 ml of water. The contents were shaken and the resulting yellow coloured solution (alkali salts of organotrithiocarbonic acids form yellow coloured solutions) was neutralised with very dilute solution of acetic acid using phenolphthalein as indicator. Diphenylcarbazide indicator (0.5 ml) was added to each solution which was titrated at room temperature (24°) with standard (0.0125 *M*) mercury(II) acetate solution to the appearance of blue colour. From the volume of titrant used corresponding to the end-point in each titration, the amount of each mercaptan was calculated. Results are given in Table 1.

Results and Discussion

The methods involving mercury(II) reagents have quite extensively been used for the determination of organosulphur compounds. The present communication extends the use of such methods to organotrithiocarbonates. Since these compounds are conveniently prepared from mercaptans, it was considered highly desirable to investigate if the method could be extended so as to determine mercaptans after their conversion to trithiocarbonates. Mercaptan solutions turn yellow immediately on reacting with an excess of carbon disulphide in presence of an alkali, indicating the formation of organotrithiocarbonate (alkali organotrithiocarbonates form yellow solutions). The transformation of mercaptan to trithiocarbonate is immediate. The quantitative nature of this transformation has already been shown by Verma *et al*[3,7] and once again by the high accuracy attained in the determination of mercaptans by this method. The excess of carbon disulphide does not interfere in the analysis of mercaptans. Both organotrithiocarbonates and mercaptans (after conversion to trithiocarbonates) have been successfully titrated with mercury(II) in aqueous medium in *p*H range 7.5-8.5 using diphenylcarbazide indicator to the appearance of blue colour. The overall standard deviations calculated from the pooled data of all the titrations performed with 5 and 12 mg of each trithiocarbonate have been found to be ± 0.063 and 0.090, respectively (Table 1). The same for 4 and 10 mg of each mercaptan are ± 0.064 and 0.089, respectively (Table 1).

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Determination of Copper in Steel, Brass, Gunmetal Nickel-Silver and Aluminium Alloy by Extraction with Phenanthraquinone Monothiosemicarbazone

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IN this communication we propose a rapid and selective method for the spectrophotometric determination of copper in ferrous and non-ferrous alloys using phenanthraquinone monothiosemicarbazone (PQMT) as the chromogenic reagent

(synthesized by the reported method[1]). The orange red coloured copper-PQMT complex extracted into choloroform from an acetate buffer solution of *p*H 5.5, absorbs at 540 nm and facilitates determination of copper in presence of a large number of cations.

Several solvent extraction methods for the extractive spectrophotometric determination of copper are known and a number of chelating agents[2-20] have been used for the purpose. However, these methods have some limitations, incomplete extraction[2,8], longer extraction period[6-10,21], a large number of interferences[4,5,6,7,17,18] and use of either masking agent[18] or synergetic extractant[20] may be cited as examples. The proposed method is free from these drawbacks. The method is comparable with neocuproin[17] extraction method, but the proposed method is free from interference due to chromium and phosphate.

Procedure for extraction and determination of copper : Steel sample (500 mg) is dissolved in aqua regia, evaporated nearly to dryness and then diluted to 100 ml. Brass (1 g) or gunmetal is dissolved in 10 ml of conc. nitric acid, evaporated to dryness, extracted with 4 ml conc. sulphuric acid and diluted to 250 ml. Similarly, nickel-silver (1 g) is dissolved in nitric acid, evaporated, extracted with water and diluted to 250 ml. Aluminium alloy (1 g), however, is dissolved in aqua regia, evaporated to a small volume, 10 ml conc. hydrochloric acid is added and the solution diluted to the mark with water in 100 ml volumetric flask.

An aliquot of any of the above solutions, containing 2.5 to 35 µg of copper is taken and 2 ml of 0.06% (w/v) PQMT solution dissolved in DMF and 20 ml of acetate buffer, *p*H 5.5 (1.0 *M*) are added. The mixture is extracted for only 15 sec in a 100 ml separatory funnel with two 5 ml portions of chloroform. The organic phase is collected and dried with anhydrous sodium sulphate and the absorbance of the orange-red complex is measured at 540 nm (Zeiss spectrophotometer; 1 cm silica cells) against a reagent blank prepared analogously. The results of triplicate analysis of standard samples and synthetic mixtures are reported in Tables 1 and 2.

TABLE 1—ANALYSIS OF COPPER IN STANDARD SAMPLES*

Sample	Composition	Copper content %		Relative error %
		Reported	Found	
33 d steel (NBS)	C 2.3, Si 1.68 Mn 0.68, Ni 2.88, Cr 0.82, Mn 0.48, Fe 90.3	1.54	1.52	1.3
41 brass (NML)	Pb 2.85, Zn 40.65, Fe 0.009	56.9	56.5	0.7
Gunmetal	Zn 4.4, Sn 5.8, Pb 6 3	83.1	84.0	1.07
Nickel-silver	Ni 18.2, Mn 0.27, Bi 0.6, Zn 25.8	55.1	54.7	0.6
Aluminium alloy	Ni 2.12, Mn 1.7, Fe 0.031 and rest Al	4.0	3.96	1.2

* Triplicate analysis.

TABLE 2—DETERMINATION OF COPPER IN SYNTHETIC SAMPLES*

Sample No.	Composition of mixture µg	Copper recovered %	Relative error %
1	Cu 15, Mn 1500 Al 1000, Ni 1000	98.3	1.7
2	Cu 15, Fe 1500, Ni 500, Bi 100, Mo 100	98 7	1.3
3	Cu 15, Cr 100, V 100, Mn 100, Ni 100	99.0	1.0
4	Cu 15, Zn 1000, Pb 100, Fe 100	98.3	1.7

* Triplicate analysis

TABLE 3—EXTRACTION OF COPPER(II)-PQMT BETWEEN $CHCl_3$ AND AQUEOUS SOLUTION AS A FUNCTION OF *p*H

*p*H	% Extraction	D, Distribution ratio
2	68.6	4.3
3	76.4	8.0
4	87 2	17.0
4.5	96.2	63.3
4.8-5 5	100.0	∞
5 8	85.0	14.2
6	73.6	6.9

Results and Discussion

The copper-PQMT complex (15 µg copper) extracted into chloroform from an acetate buffer solutions of *p*H 5.5 show λ_{max} at 540 nm whereas the reagent shows negligible absorbance at this wave length. The extraction of copper was studied at various *p*H (*p*H was adjusted with 1 *M* acetic acid and 1 *M* sodium hydroxide solution). The optimum extraction was between *p*H 4.8 and 5.5 and it decreased beyond this range (Table 3). The complex obeys Beer's law over the concentration range of 2.5 to 35 µg/10 ml of organic phase at 540 nm. The molar absorptivity and Sandell's sensitivity of the complex is 1.16×10^4 l. mole^{-1} cm^{-1} and 0.005 µg/cm^2 respectively. The colour of the complex is stable for 24 hr. 2 ml of 0.06% reagent and 15 sec shaking time are enough for quantitative extraction of copper (2.5 to 35 µg).

The complex is soluble in solvents such as chloroform, MIBK, *iso*-amylalcohol and ethylacetate and extracts partially in benzene and toluene. Carbontetrachloride is not suitable for extraction of the complex. For further studies chloroform was selected as it facilitates quick separation of the two phases.

Effect of foreign ions : Varying amounts of foreign ions were taken with fixed amount of copper (15 µg) and the recommended procedure was followed for extraction and absorbance measurements. Ag(I) (2 mg), Co(II) (300 µg), Zn(II) (2.5 mg), Cd(II) (1.5 mg), Mn(II) (1.5 mg), Sn(II)

(1 mg), Ni(II) (5 mg), Hg(II) (300 μg), Pb(II) (2.5 mg), Al(III) (3 mg), Bi(III) (1.5 mg), Cr(III) (100 μg), Au(III) (250 μg), Sb(III) (100 μg), Ru(III) (500 μg), Rh(III) (150 μg), Ir(III) (100 μg), Fe(III) (2 mg), La(III) (1 mg), Sn(IV) (100 μg), Pt(IV) (2.5 mg), Th(IV) (150 mg), Se(IV) (500 μg), V(V) (2 mg), U(VI) (1 mg), Cr(VI) (500 μg), Os(VI) (2.5 mg) and anions such as phosphate (150 μg), fluoride (1 mg), bromide (250 μg) and chloride (500 μg) do not interfere in the estimation of copper. Of the ions tested only palladium, tellurite, tartrate, citrate, ascorbate and EDTA showed interference.

The standard deviation of the mean absorbance for 15 μg of copper was found to be 0.006. The method has thus good precision.

Composition of the complex : The composition of the coloured complex was found to be 1 : 2 (metal to ligand ratio) by Job's continuous variation[22] and the mole ratio method[23]. The dissociation constant K, of the complex was evaluated by the expression

$$K = \frac{(m\alpha C)^m (n\alpha C)^n}{C(1-\alpha)}$$

where m and n are the number of metal ions and ligand molecules in complex, C is molar concentration and α is the degree of dissociation.

$$\alpha = \frac{Am - As}{Am}$$

where Am and As are maximum absorbance (extrapolated value) and absorbance at stoichiometric molar ratio. The dissociation constant of the copper-PQMT complex was found to be 2.16×10^{-10}.

Conclusion : The proposed method for photometric determination of copper with phenanthraquinone monothiosemicarbazone is new, rapid and selective. The results are accurate and the wide applicability of the method has been demonstrated by the satisfactory analysis of synthetic mixtures and standard samples.

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Professor Santi R. Palit Memorial Fund

AN APPEAL

Professor Santi R. Palit, the renowned Physical Chemist and Polymer Scientist and a past Vice-President of the Indian Chemical Society expired on September 13, 1981. To perpetuate the memory of the Late Professor, his numerous students, colleagues, friends and admirers has decided, in a recent meeting, to create a Fund to be named "Professor Santi R. Palit Memorial Fund," for instituting either an Annual "Seminar Lecture" on regional basis to be delivered by an eminent Indian scientist in the field of Physical Chemistry or an Annual cash award to be called "Palit Award" to be given to an Indian scientist for significant original contribution in the field of Polymer and/or Physical Chemistry. It is aimed to raise a fund of about Rs. 2,50,000/- and to make available a sum of Rs. 10,000/- every year for the Lecture or the Award. The operation of the Fund and the selection of the Lecturer or the Awardee will be entrusted to suitable bodies like Indian National Science Academy, New Delhi ; Council of Scientific and Industrial Research, New Delhi ; Department of Science and Technology, New Delhi ; Indian Chemical Society, Calcutta or Indian Association for the Cultivation of Science, Jadavpur, Calcutta.

The Fund is being raised by Prof. S. R. Palit Memorial Committee, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032. Efforts are being made to get the Fund registered and contribution to the Fund exempted from Income Tax.

Professor S. R. Palit Memorial Committee fervently appeals to all for a generous contribution to the Fund so that the memory of this outstanding scientist is perpetuated in a befitting manner.

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